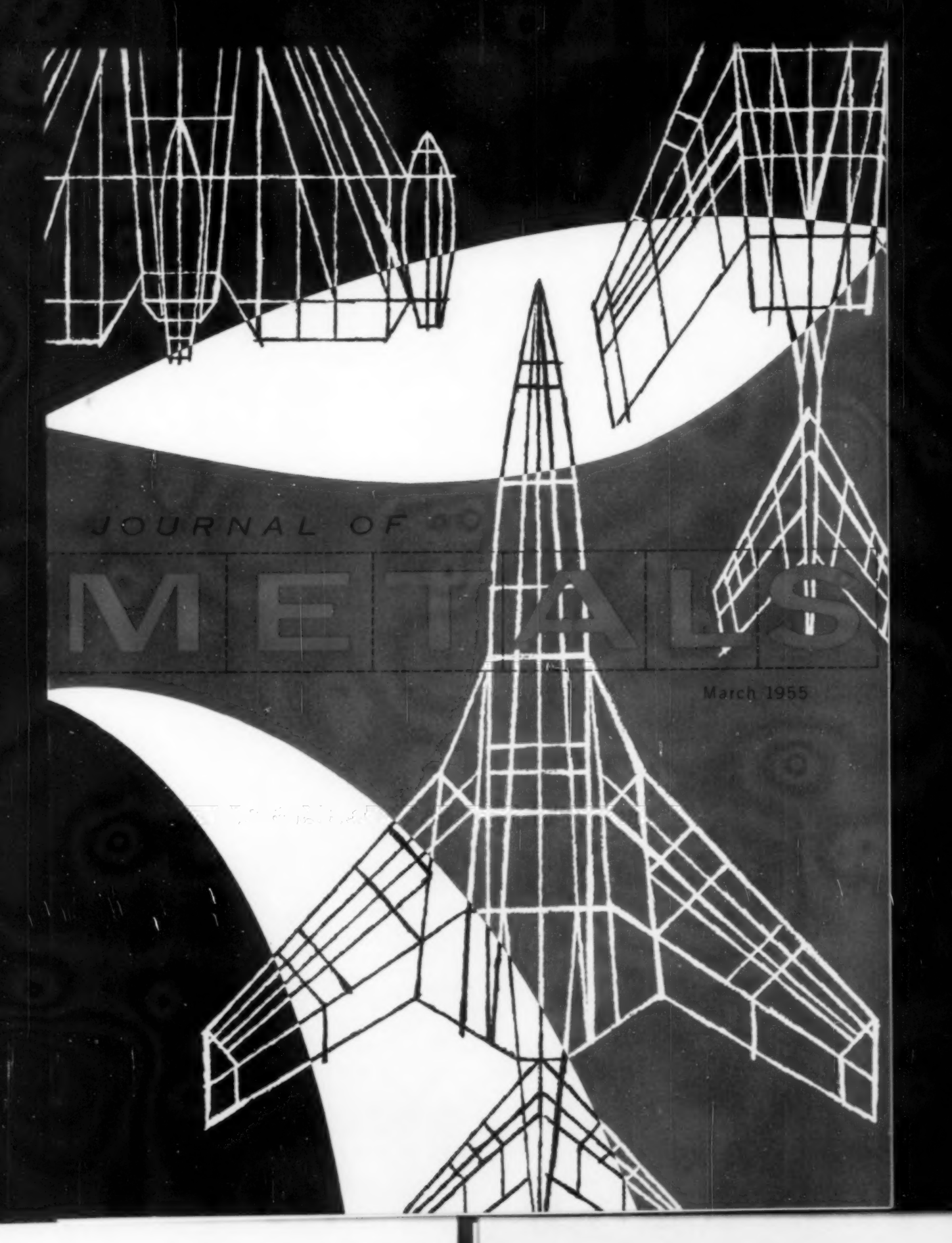
JOURNAL OF
METALS
March 1955

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JOURNAL OF

METALS

Published to provide a continuing, authoritative, and up-to-date record of technological, engineering, and economic progress in all branches of the metals industry by the
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COVER

Harry Brocke's theme for this month's cover is drawn from the articles on the use of titanium in aircraft beginning on p. 443.

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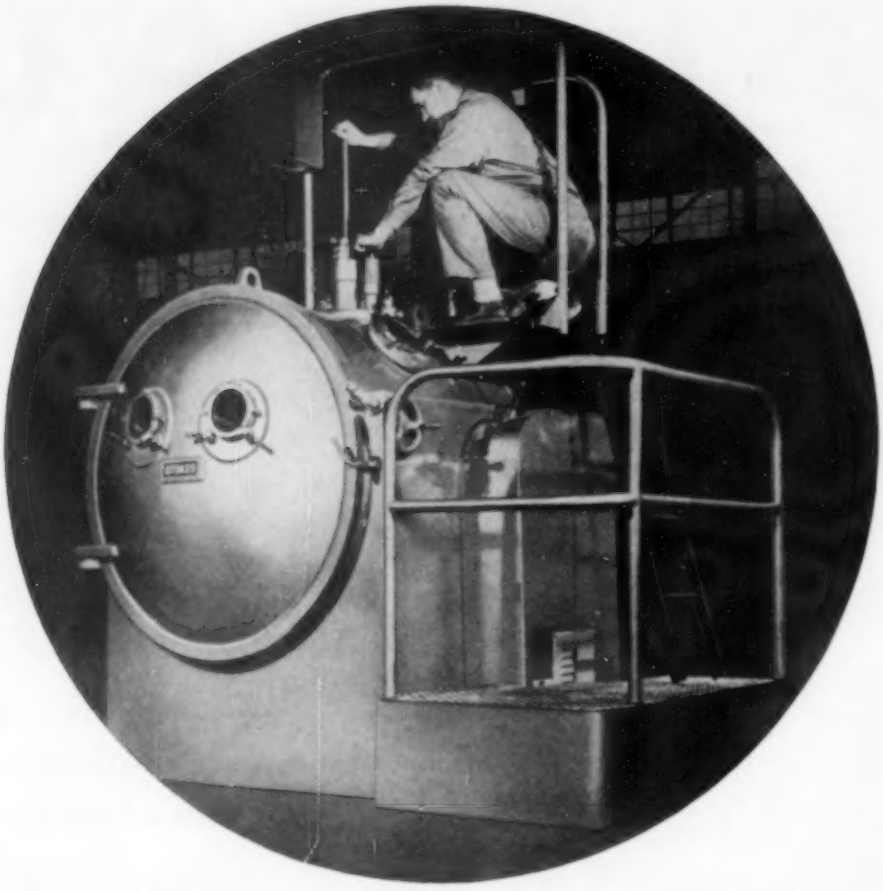
STOKES ANNOUNCES



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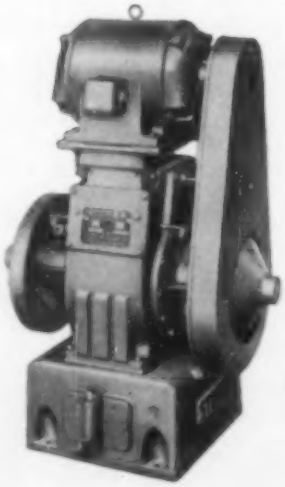

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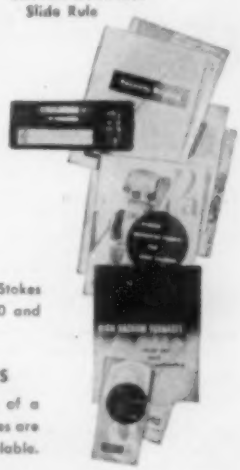
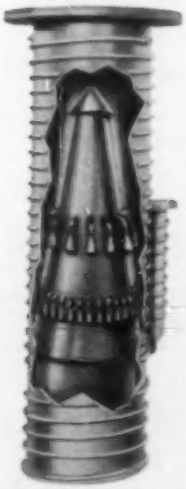
SEND FOR TECHNICAL LITERATURE:

- Microvac Pumps—Catalog 730
- Diffusion and Booster Pump Specification sheets and performance curves
- The Story of the Ring-Jet Pump
- Complete Vacuum Processing Systems—Catalog 730
- How to Care for Your Vacuum Pump—Booklet 755
- Vacuum Impregnation—Catalog 760
- Vacuum Drying—Catalog 720
- Vacuum Furnaces—Catalog 790
- Vacuum Metallizing—Catalog 780
- Vacuum Calculator Slide Rule



VACUUM EQUIPMENT



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Industrial Notes

• The growing significance of graphite in electrometallurgy and electrochemistry is described in a brochure recently issued by the Electrode Div., Great Lakes Carbon Corp. In addition to the importance of electrode dependability, the brochure outlines Great Lakes production methods. The publication is free upon request to Great Lakes Carbon Corp., 18 East 48th St., New York 17, N. Y.

• Carborundum Co. established a new operating unit, the Electro Minerals Div., to manufacture and sell silicon carbide and fused alumina crudes, abrasive grain and related electric furnace products in the U. S. Joseph S. Imirie, formerly assistant to the president, will be general manager of the new division.

• Newport Steel Corp. formally opened its new reversing cold reduction mill January 26 with the start of regular production. The new mill was installed as the major item in a $9 million expansion program for further diversification of Newport products. The facility is equipped to reduce hot rolled pickled steel in coil to desired gage in widths up to 48 in. for shearing and further processing into cold rolled sheets. Erection was by Merritt-Chapman & Scott's industrial and building construction div.

• The largest movable head flattening press ever built was unveiled at the Lukens Steel Co. plant in Coatesville, Pa. The new press has a movable head never achieved before with a capacity of 5000 tons pressure. Designed and constructed by Clearing Machine Corp. of Chicago, the press will be used for straightening armor plate prior to naval shipyard delivery. It will also be used by Lukens for commercial purposes. One unusual feature of the press is the ability of the pressing head to be moved from right to left a total of 160 in.

• International Nickel Co. of Canada, Ltd., made the first shipment of about 450,000 lb of nickel to the Central Services Administration under a contract signed between the company and the U. S. agency last fall. The contract calls for delivery of a minimum of 4.5 million lb of refined nickel by August 1955, from certain nickel concentrate produced by Sherritt Gordon Mines Ltd.

• Construction is scheduled to start immediately on a 100-in. cold mill and supporting equipment for finish rolling wide aluminum coiled sheet at Aluminum Co. of America's Davenport Works. Cost is fixed at more than $5 million. Installation of the new mill will be made in existing buildings, with operation expected in 1956.

• The du Pont Co. announced a fund of $291,000 for grants to universities and colleges to help improve the teaching of science and mathematics as part of its $800,000 aid-to-education program for 1955-56. There are three separate parts to the support to teaching: $75,000 for summer and winter fellowships for master's degree training for high school science and mathematics teachers; $125,000 to advance the teaching of chemistry in 50 privately supported institutions, mostly liberal arts colleges; and $91,000 for 24 postgraduate teaching assistantships in chemistry.

• Applications for the 1955-56 sessions of the Oak Ridge School of Reactor Technology are now being accepted. Enrollment for the 50-wk course beginning in September closes Mar. 14, 1955. Accepted students will participate in an advanced curriculum, which includes classified details of reactor technology. Additional information, including the school's bulletin and application forms, may be obtained from The Director, Oak Ridge School of Reactor Technology, Post Office Box P, Oak Ridge, Tenn.

• Carborundum Co. has issued a 24 page booklet giving the latest physical and chemical properties on super refractories by Carborundum. Data is assembled in easy to find style and augmented by lists of applications together with pertinent charts and tables. *Properties of Super Refractories* can be obtained from Refractories Div., Carborundum Co., Perth Amboy, N. J.

Coming Events

Mar. 1, AIME, Northern Ohio Section, NOHC, Pick-Ohio Hotel, Youngstown, Ohio.

Mar. 1-3, National Assn. of Corrosion Engineers, University of Tennessee Corrosion Conference, Knoxville, Tenn.

Mar. 9, AIME, Connecticut Local Section, Bridgeport, Conn.

Mar. 10, AIME, Cleveland Local Section, American Room, Manger Hotel, Cleveland.

Mar. 10-11, Porcelain Enamel Institute, Pacific Coast conference, Biltmore Hotel, Los Angeles, Calif.

Mar. 14-15, Steel Founders' Society of America, annual meeting, Drake Hotel, Chicago, Ill.

Mar. 15, Society for Applied Spectroscopy, Philadelphia Section, Philadelphia, Pa.

Mar. 16, AIME, Connecticut Local Section, annual meeting, Statler Hotel, Hartford, Conn.

Mar. 20-23, American Institute of Chemical Engineers, Kentucky Hotel, Louisville, Ky.

Mar. 29-Apr. 1, Western Metal Exposition, Western Metal Congress; Pan-Pacific Auditorium, Ambassador Hotel, Los Angeles, Calif.

Apr. 13, Material Handling Institute, spring meeting, Drake Hotel, Chicago, Ill.

Apr. 14, AIME, Cleveland Local Section, joint meeting with American Ceramic Society, NACA Laboratories, Cleveland Hopkins Airport.

Apr. 16, ASME, organization anniversary meeting, Stevens Institute of Technology, Hoboken, N. J.

Apr. 18-20, Third National Air Pollution Symposium, Huntington-Sheraton Hotel, Pasadena, Calif.

Apr. 18-20, AIME, Blast Furnace, Coke Oven and Raw Materials and National Open Hearth Steel Conferences, Bellevue-Stratford Hotel, Philadelphia, Pa.

Apr. 19-22, ASME, spring meeting, Lord Baltimore and Southern Hotel, Baltimore, Md.

Apr. 19, Society for Applied Spectroscopy, Philadelphia Section, Princeton University, Princeton, N. J.

Apr. 19-21, Canadian Institute of Mining and Metallurgy, annual meeting, Royal York Hotel, Toronto.

Apr. 22-23, AIME, New England Regional Conference, Boston, Mass.

Apr. 28-30, AIME, Pacific Northwest Conference, Spokane, Wash.

May 1-4, American Institute of Chemical Engineers, Shamrock Hotel, Houston, Texas.

May 2-6, Electrochemical Society, Sheraton-Gibson Hotel, Cincinnati, Ohio.

May 6, American Assn. of Spectrographers, annual conference, Chicago.

May 10-12, Metal Powder Assn., Bellevue-Stratford Hotel, Philadelphia, Pa.

May 14-22, Chemical Engineering & Equipment Exhibition, Frankfort-am-Main, Germany.

May 16-19, American Mining Congress, coal convention and exposition, Public Auditorium, Cleveland, Ohio.

May 1, -30, Porcelain Enamel Institute, midyear div. conference, Edgewater Beach Hotel, Chicago, Ill.

May 19, AIME, Utah Local Section and University of Utah Student Chapter, joint meeting.

May 30-June 1, Chemical Institute of Canada, annual conference, Quebec, Canada.

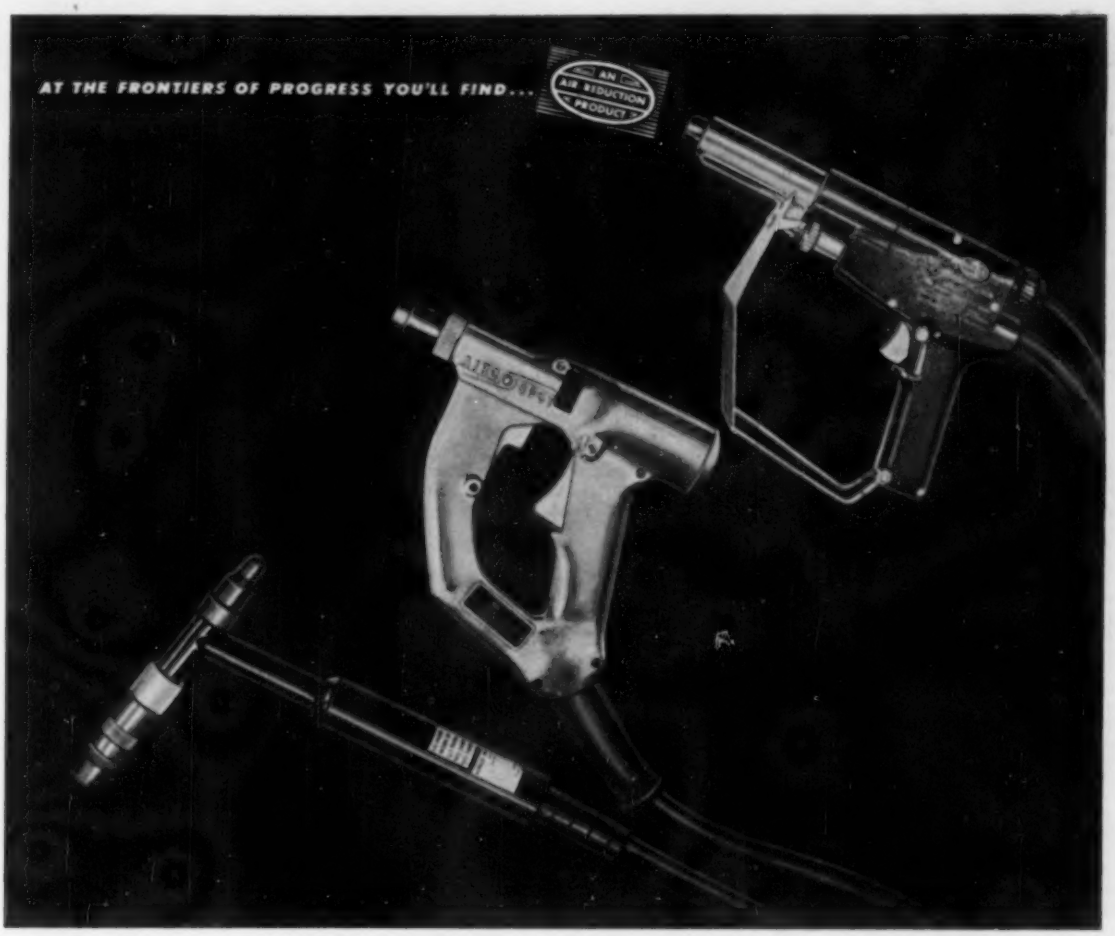
May 31, World Power Conference, International Executive Committee, Paris, France.

June 1-18, Joint Metallurgical Societies, European meeting.

June 20-23, Industrial Finishing Exposition, Cleveland Public Auditorium, Cleveland, Ohio.

June 20-24, American Society for Engineering Education, annual meeting, Pennsylvania State University, State College, Pa.

June 26-July 1, ASTM, annual meeting, Chalfonte-Haddon Hall, Atlantic City, N. J.



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Test Engineer, mechanical or metallurgical engineering graduate with aircraft accessories experience for product testing of airframe fastening devices. Must have stress analysis experience. Salary open. Location, New Jersey. W980.

Plant Manager, 40 to 50, with good background, to head up production, production control, purchasing, industrial engineering, quality control, materials handling and traffic in a division of 1000 employees. Should have experience in sheet metal fabrication on such products as furnaces and aircraft accessories, with both high production and job shop operation. Salary open. Location, Midwest. W971.

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Research and Development Engineer, graduate metallurgical or chemical engineer, with some experience in hydrometallurgical or inorganic chemical processing; will consider a recent graduate who is interested in these fields. Salary, $4500 or more a year. Location, Texas, W901.

Powder Metallurgist, familiar with powder metallurgy practice, good imagination and sound scientific knowledge, to develop new aluminum base alloys, especially with improved strength at elevated temperatures. Will immediately or eventually take charge of all powder metallurgy projects. Permanent. Salary open. Location, Northwest. S422.

Senior Metallurgist, graduate, 30 to 37, with experience in mineral dressing and extractive metallurgy, including sulphide flotation, for research and development laboratory. Must be able to work under limited supervision and willing to travel to operating plants to assist with metallurgical problems. Permanent. Salary open. Location, California. S140.

Metallurgist, up to 32, recent graduate or better. Knowledge of steel mill operations desirable. Will be trained for management work in steel mills. Salary, $4560 to $5151 per year. Location, south Chicago. C2555(b)

Plant Manager, 40 to 55, to assume full responsibility for factory operations, industrial engineering, production and material control, quality control, purchasing and plant engineering for the manufacturer of small auto heaters. Must have had at least 5 years experience in plant management at top level covering both mass and job steel and metal fabrication. Must have knowledge of planning and controlling all phases of manufacturing. Salary, $15,000 to $20,000 a year. Location, Indiana. C2550(a)

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Books for Engineers

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Basic Engineering Sciences, by William Glendinning. $3.00, 126 pp., 1954. —Problems with solutions selected from Part II of New York State examinations for engineer-in-training and professional engineer 1945 to June 1954 are given. Various aspects of hydraulics, thermodynamics, machine design, and electrical principles and equipment are covered.

Development of the Guided Missile, second edition, by Kenneth W. Gatland. *Philosophical Library, Inc.* $10.00, 292 pp., 1954.—The book is a survey of the evolution of guided missiles up to the present time and a description of their possible future development. Methods of propulsion of rockets and ram jets, current methods of research, military and peaceful applications of various types of missiles are among the subjects discussed. Consideration is also given to rockets for high altitude research, space satellites, and interplanetary flight. Comparative data on 140 rockets from eight countries and scale photographs of more than 40 notable rockets are given.

Jet—The Story of a Pioneer, by Frank Whittle. *Philosophical Library, Inc.* $6.00, 320 pp., 1954.—This is an autobiographical account of the development of the world's first successful jet plane, the Gloster/Whittle E.28/39. The author describes his first concept of the turbo jet engine, his efforts to arouse interest in his ideas, and the difficulties his company encountered with British government officials. He records in nontechnical language the engineering problems faced in designing, manufacturing, and testing an experimental engine, and in developing improved types.

Storage Batteries, fourth edition, by George Wood Vinal. *John Wiley & Sons, Inc.*, $10.00, 446 pp., 1955.—The fourth edition of this book has been largely rewritten to conform with the many changes that have taken place in battery design and construction in the past 14 years. The book emphasizes the scientific principles of storage batteries without allowing the treatment to become too highly technical. Physical and chemical properties of the materials used in battery manufacture are discussed, and the reader is given a general description of battery manufacturing. Industrial applications are described.

Annual Review of Nuclear Science, Vol. 4, edited by James G. Beckerley. *Annual Reviews, Inc.* $7.00, 483 pp., 1954.—The present volume contains 17 papers that are essentially surveys of the literature on recent developments, including extensive reference lists. There are papers on different aspects of nuclear particle detection, penetration of heavy charged particles in matter, radioactivity in geology and cosmology, and on various other topics. Author and subject indexes are included.

Make It With Aluminum. *Fawcett Publications, Inc.* 75¢, 145 pp., 1955.—The book explains in detail how to work with, and what can be made with do-it-yourself aluminum. It contains instructions on how to work with the metal with standard woodworking tools.

Control of Emissions from Melting Operations. *American Foundrymen's Society.* $2.25, $1.50 to AES members. 1955.—Information contained in this booklet will provide foundry management with a valuable guide to the steps necessary for control of air pollution in a manner that the plant may continue to operate and comply with local air pollution ordinances now in effort or forthcoming.

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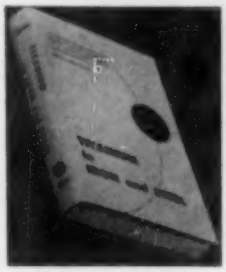

This is the only book available that reviews and correlates all the important data in world literature on titanium as an alloying element in iron and steel. Nearly 300 papers (listed in the bibliography at the end of the book) were reviewed for the manuscript.

Opening with a general discussion of titanium — its principal sources, concentration, preparation, etc. — the book goes on to examine the properties and effects of the element when alloyed with cast iron and steel. Its deoxidizing effects are treated in full. Special emphasis is placed on its unique effects in stabilizing nitrogen and in fixing carbon in alloys where other carbides may be undesirable, and on its usefulness in steel which is to be enameled, and in certain complex ferrous alloys for high-temperature applications.

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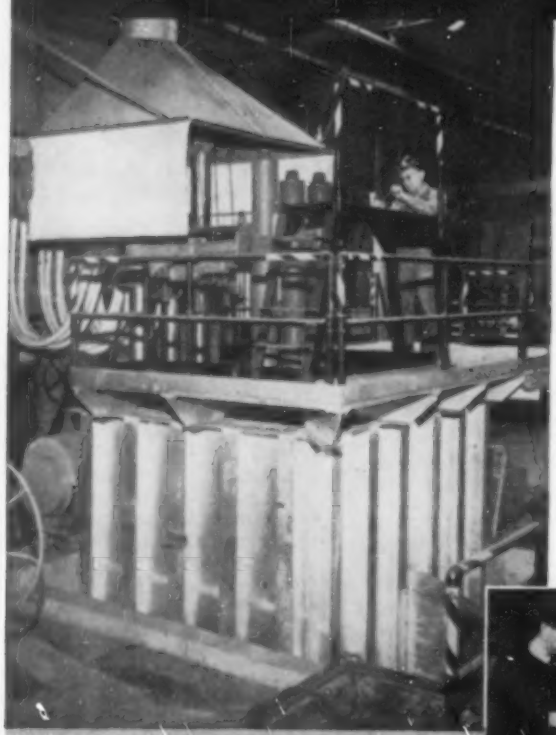
Lectromelt **furnaces are important tools in this work**

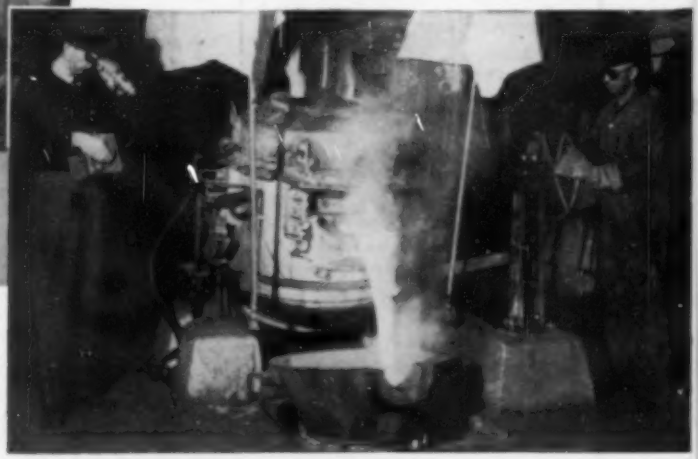


BOULDER CITY, NEVADA

In this 500-KVA Lectromelt-equipped furnace, development work started in a smaller Lectromelt-equipped electric furnace is continued. Problems include the evaluation of agglomerated domestic chromite concentrates for production of ferrochrome, and research on production of ferromanganese from off-grade concentrates.

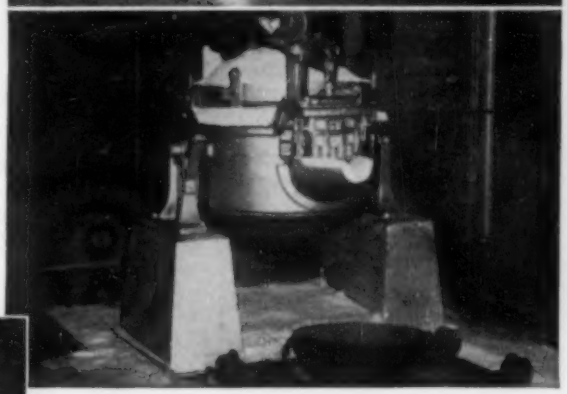
SALT LAKE CITY, UTAH

After new ideas have been tested in a smaller Lectromelt Furnace, they are stepped up to a pilot plant basis in this Type U Lectromelt Furnace. Here smelting rates, power and electrode consumption and refractory life can be determined. Problems have involved the smelting of low-grade nickel ores, of titaniferous magnetite ore, manganese concentrates and of rhodonite.



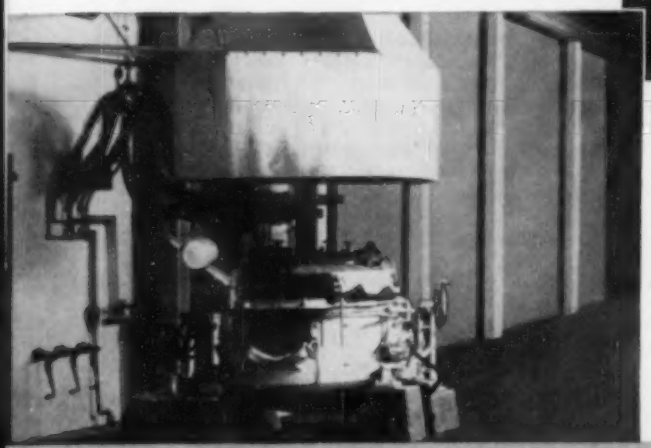
ALBANY, OREGON

A Type W, single-phase Lectromelt Furnace is used for preliminary smelting tests. A Type ST, 3-phase Lectromelt Furnace melts and refines metals and alloys produced in a continuous electric smelting furnace of the Bureau's own design. This picture shows refined cobalt being poured into water to granulate the metal to meet GSA specifications.



ROLLA, MISSOURI

This 100-KW Lectromelt Furnace is used for pyrometallurgical investigations such as these: Processes for separating titanium oxide from ilmenite or rutile ores . . . for separating cobalt, copper and nickel from a complex matte, or as a combined smelter-converter in extracting these metals from a pyrite concentrate . . . in experimental smelting of low-grade iron ores.



PITTSBURGH, PENNSYLVANIA

The Pyrometallurgy Laboratory of the U. S. Bureau of Mines will soon install this Type ST Lectromelt Furnace (originally located at the Bureau's Redding, California Station) to enlarge the Pittsburgh Laboratory's research facilities.

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*Reg. T. M. U. S. Pat. Off.

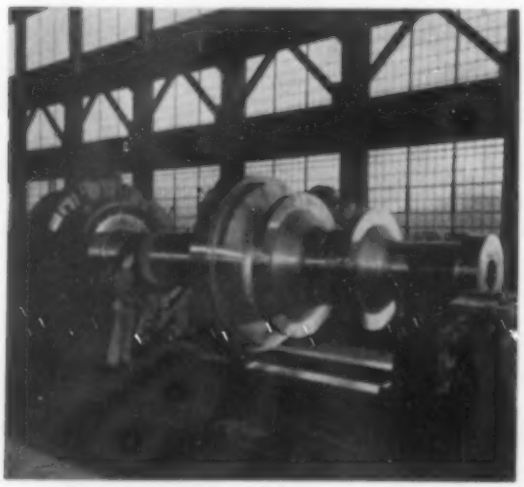
WHEN YOU MELT... MOORE RAPID *Lectromelt*

NO one can fix an exact date for the Industrial Revolution. The revolution was the sum of many things—not the result of the creation of one new industrial machine. In the same way no point in time can be assigned for the age of automation. Some believe that it has already started. Probably so. That exact dates cannot be fixed for either the Industrial Revolution or the automation era is unimportant.

What is important is the thinking preceding the arrival of a society whose productive facilities will be totally automatic. The Industrial Revolution was entered into with little or no thought of what it would mean in terms of its effect on human beings. It enveloped the world before anyone realized its existence. Engineers, scientists, inventors, and industrial leaders are quite aware of what automation can mean. It has become almost impossible for modern man to avoid the social implications of any of his acts.

The prediction is that 20 million new jobs will be needed between 1955 and 1975 to occupy the 85 million persons expected to compose the working force within the near future. It ties in with the predicted 221 million population by 1975. Thus the old Malthus theory of whether the supply of goods can keep up with the population growth is being rewritten to read can the supply of jobs keep up with job applicants. Industrial Psychology, Inc., national pyschological research organization, sees automation definitely complicating things. The electronic revolution "sees the machine replacing the workers' brain in office and factory." Whether it will result in increased productivity and creation of new jobs in building and maintaining new machines, or add more employables with no place to go in the labor market, the psychology group says, is a moot question.

Some conclusions can be drawn right now. Starting in 1955, and intensified by 1960, management will have a greater selection of applicants. Another implication, again according to Industrial Psychology, Inc., is that employers will have to take a more critical look at present work force, weeding out inefficient performers lacking basic pyschological traits to do a better job. The research center's attitude is that employers might be doing those employees a favor—job hunting in the 1960's may be tougher than it is now.



This giant shaft made of carbon vanadium steel and weighing 61 tons is to be used in the $70 million Gavins Point power and flood control project on the Missouri River, S. D. The rough turned shaft is on a boring lathe at the Bethlehem, Pa. plant of Bethlehem Steel Co. The shaft is 22 ft long and its largest flange exceeds 8 ft in diam.

INDUSTRIAL use of radioisotopes has been somewhat stymied by the lack of enough adequately trained personnel or training centers. Only a small number of trainees can be handled by the Oak Ridge Institute of Nuclear Studies. With this limitation in mind, 14 New Jersey firms who believe in the future of radioisotopes as tools of production have contributed $1000 each to setting up the Radioisotope Center at Rutgers University. The contributions will help defray capital expenditures for the relatively expensive counters, handling devices, and protective measures needed for the Center. Total initial cost is estimated at $30,000. Additional memberships are needed, although the University has inaugurated the first class.

Courses will be designed to provide basic understanding of radioisotopes and their use. The general direction of the Center is under an advisory committee made up of industry and university representatives. Frank G. Dunnington, Rutgers physics professor, is committee chairman.

Dr. Dunnington points out that the membership fee is primarily a contribution to the University for work in the field of radioisotopes, but direct and immediate return to the companies will be priority in the selection of students for training. Thirty-two students were accepted for the first course, conducted on the graduate level in cooperation with the Rutgers dept. of physics and School of Chemistry. Course instructors are Seymour T. Zenchelsky, assistant professor of analytical chemistry, and Peter Lindenfeld, instructor in physics. Students will pay the standard university tuition fee of $44 for New Jersey residents and $56 for out-of-state applicants.

The 14 firms contributing $1000 for industrial membership are: central research laboratories of the American Smelting & Refining Co.; E. R. Squibb & Sons, div. of Olin-Mathieson Chemical Corp.; Standard Oil Co.; Campbell Soup Co.; Bakelite Div. of Union Carbide & Carbon Co.; Johnson & Johnson; Johns-Manville Products Corp.; Hoffman-LaRoche, Inc.; Hercules Powder Co.; Sacony Vacuum Laboratories; Radio Corp. of America Laboratories; Calco Chemical Div., American Cyanamid Co.; General Foods Corp.; and Ciba Pharmaceutical Products, Inc.

THE Joint Committee on Atomic Energy of the Congress recently heard Commissioner Thomas E. Murray say that, "I am of the opinion that during the past year the Commission has lost some of the stature it previously enjoyed."

He pointed to the Dixon-Yates controversy as the chief unhappiness within the AEC. He denied the validity of the argument that the contract is "merely an extension—and indeed an improvement—on a pattern which I established, namely, that of using combinations of private utilities to meet the exceptionally large power requirements at AEC installations."

Mr. Murray has previously testified that he is responsible for the establishment of the pattern of which Dixon-Yates is said to be part. "The argument is a specious one," Mr. Murray told the joint committee. "The Dixon-Yates contract, and the OVEC and EEI contracts, with which it is compared, are similar only with respect to the means of obtaining power. The 'Ohio Valley' and 'Electric Energy' contracts were instituted to fill the urgent and direct need at AEC installations for electric power to meet military requirements."

Commissioner Murray stated that the Dixon-Yates combination is an attempt to meet the civilian commercial needs in the Memphis, Tenn., area, hundreds of miles from the nearest AEC installation. He testified that he signed the contract last October because he believed "quick deposition of this matter by the Commission was in the public interest." He hoped that the signing of the pact would free the Commissioners and their staff from protracted deliberations and permit them to devote their energies to other primary responsibilities. He regrets that that hope has not been fullfilled.

Mr. Murray placed considerable emphasis on the need for maintaining the complete confidence and trust between the Commission and the Joint Committee. In another part of his statement he noted that industrial atomic energy would become a reality in proportion to the importance attached to the program. Following the commissioner's statement before the Congressional Committee, Lewis Strauss, AEC chairman, clashed with Mr. Murray for the third time within recent weeks. Mr. Strauss introduced some four packing cases filled with papers concerning Dixon-Yates, in a move to discredit the contention that the Commission had passed on the contract with little thought. Washington observers were noting that the AEC, for a long time something of a sacred cow, was not all sweetness and light.

◆◆◆◆◆◆

ONE of 1954's most spectacular statistics has to do with the sharp decline of England's iron and steel imports. The country's steel industry has been almost fantastically successful in reaching at least part of its many goals. Exports also showed an improvement with 1954 shipments totaling 2,355,160 tons, compared with 2,112,360 tons in 1953. With Commonwealth nations getting a 6 pct preferential rate, imports to those countries have shown a natural increase. Australia alone imported 331,730 tons last year, an increase of 206,505 tons from 1953.

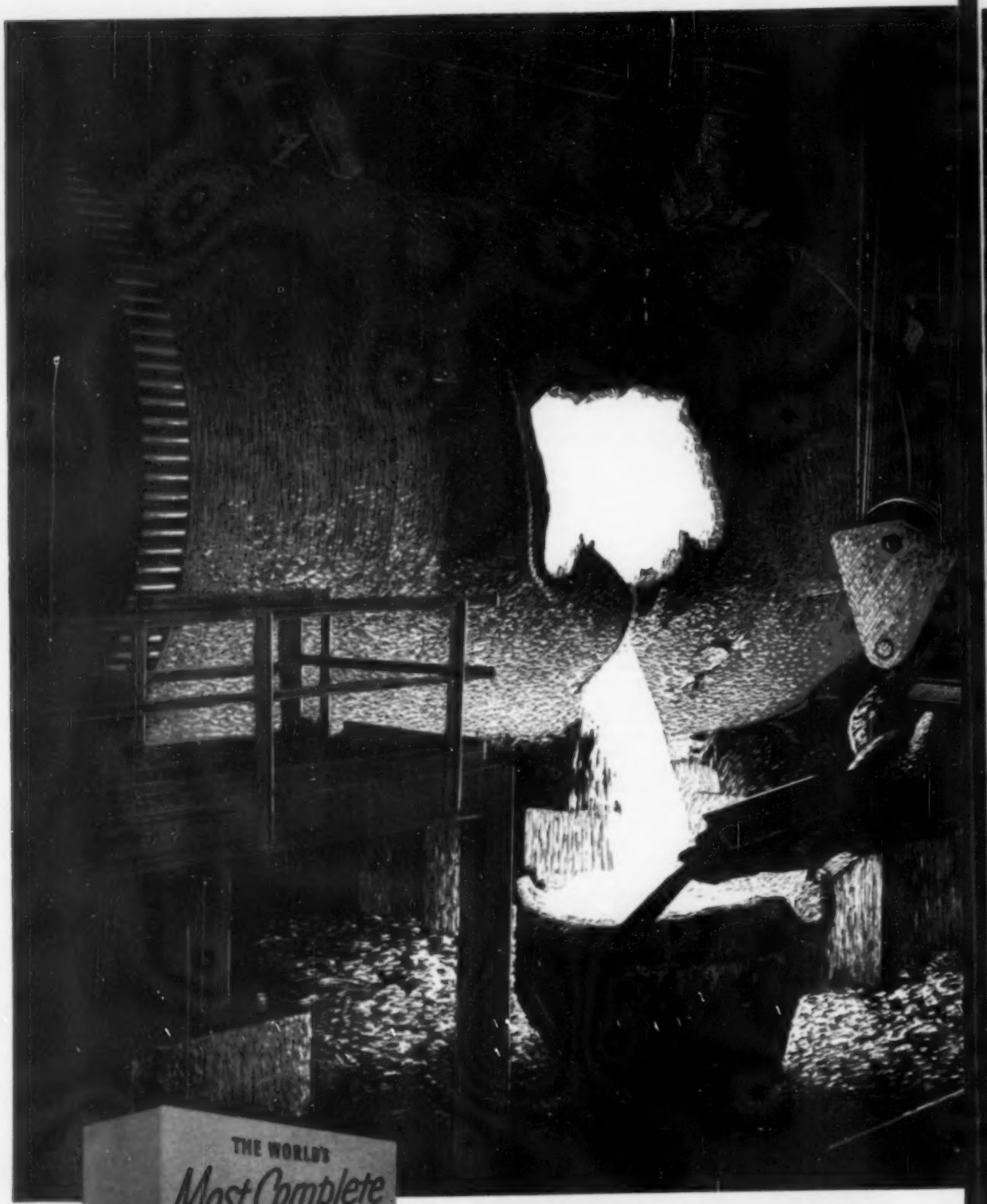
A large source of radioactive cobalt was recently shipped from Oak Ridge National Laboratory, operated for the Government by Union Carbide & Carbon Corp. The Cobalt —60 source was placed in this 6550 lb shield by remote control and is shown being removed from the radioisotope dept.'s "hot cell." Babcock & Wilcox Co., Barberton, Ohio, is going to use the cobalt source for radiography work.

New Zealand bought some 198,902 tons from the mother country, compared with 112,168 tons the previous year. On the other side of the book England is still not producing enough pig iron to meet her needs. In 1953 she imported about 693,594 tons. Last year the figure dropped to 339,278 tons in 1954 but still represented a substantially high level of dependency upon foreign sources. Several blast furnaces expected to be blown in this year may remedy the situation.

Sheet imports increased enormously, in line with the huge increase in the motor industry's activity. With the motor industry expected to invest about $280 million in expansion programs, the demand for sheet will probably stay high. The expected sheet demand has served as ammunition for those who want another strip mill in the country.

One of the most unusual aspects of the decline in imports was the falling off of semi-finished products from 420,681 tons to 70,207 tons. Low imports continued throughout the last few months of 1954 at a time when re-rollers were at peak capacity and the supply of semi-finished products was extremely tight.

With all heavy steel plants working under what is termed "extreme pressure" all kinds of records are looked for. Consumer demand has been high and is expected to stay that way. Additional demands will be made within the next few years from a £1.2 billion railroad development program announced by the British Transport Commission.



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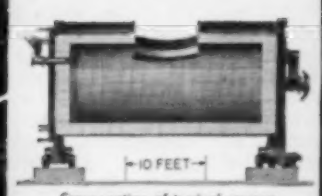

Cross-section of typical copper converter, showing refractory lining.

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Drift of Things

RECENTLY, the AIME publications office at 29 West 39th St. went through a space reorganization. Things and people had to be realigned to bring about a better flow of advertising matter, editorial copy, and the less exciting business details of publishing. The biggest problem was not the reorganization or reorientation of people, but of inanimate objects like files, book cases, and a mountain of miscellaneous records. After discarding much whose reason for being had long ago been lost, much still remained. Following a lot of planning, replanning, pushing, moving, and removing, a kind of logic was established—for the present anyway.

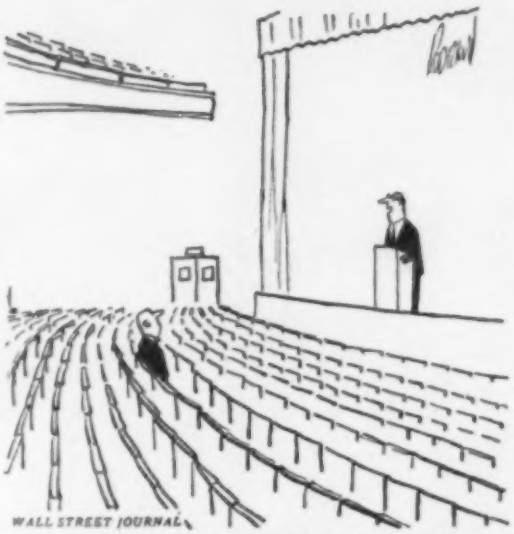
But the specter of what the future holds still lies in some recess of the collective mind of the publications staff. The files—would they ever stop growing? The answer seems obvious—never. The reason is that file cabinets have a loneliness that can never be satisfied. They develop a kind of personality—one which constantly cries for more company, until the number of file cabinets resembles a green legion that slowly forces humans into a little corner without light or air. Plans for the new Engineering Societies building offers some hope of rescue. But if one allows his mind to ramble a bit a harrowing picture is conjured up. Someday, unless the world comes to terms with its mounting repositories of knowledge, the mass of information is likely to become so unwieldy that much of it will be lost under a mass of paper, filing cabinets, books, and library catalogs.

Since man first began showing signs of being on the upper level of the animal world he has been collecting various bits of information. And from the start had trouble with synthesizing and absorbing information into his frame of reference. Wars, famine, and the like have contributed to the confusion. One of the most crucial periods of the fight to preserve knowledge came during the so-called Middle Ages, actually a transition from the Greco-Roman world to the Renaissance. If not for the Church, and certain Arab and Hebrew philosophers, most of the Greek heritage would have been lost. As it was, barbarian hordes that swept across Europe from Asia managed to destroy many irreplaceable libraries.

Vannever Bush, in a recent address before the American Society of Mechanical Engineers at their Founding Anniversary Meeting, summed up the probelm posed by the gigantic mass of accumulated data in two sentences.

"The problem is not essentially one of techniques. It is rather one of deciding who is to do the job of clearing up the confusion and under what auspices."

The techniques are available. There are at least, according to Dr. Bush, 50 companies already active in the production of various kinds of data handling equipment. They range from microfilm devices to electronic units motivated by pale little cards with peculiar arrangements of little holes. Government may be the proper agency to do the job of cataloging information. But can a machine already jammed with millions and millions of reams of paper be expected to do a job that in itself threatens to engulf it? The selection of means alone could engulf Government in another sea of paper—this time in form of reports on how best to handle the problem.



". . . some of us would view the subject '*resiliency of painted metals*' as one lacking of interest . . ."

But Dr. Bush has faith. He feels the world will find a solution and that mastery of man's record will someday be achieved. Communication is the life of democracy. Thus, if free people are to survive they must find a way to turn all their information resources into a mobile instrument. If they fail, man would most probably lose his greatest gamble.

M. A. M.

A COMMITTEE composed of the Presidents of the AIME, ASCE, ASME, AIEE, and AIChE, has recommended to the respective societies that the new Engineering Societies Building be located in Pittsburgh. This decision came after a complete review of cities of interest, taking all factors into account. All that remains now is for the individual societies to approve the recommendation, and we're practically on our way. Of course, there are also a few minor details that will have to be taken care of —such as selecting a building site, choosing the type and size of building desired, and arranging for the erection of the building.

There is a very noticeable lack of hustle and bustle among the individuals and organizations involved. Over the years, there have been so many decisions made concerning a new engineering building, that one more is taken in stride. Few people actually believe that the final site will be Pittsburgh, and an overwhelming majority believes that all societies will remain at the present site until the building begins to cave in. We aren't sure just what to believe, but if you know of any small homes that will be available in Pittsburgh in about 2 years----------

A. S. Cohan

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As to the savings they assure, note this: The U. S. Navy reports that over a 5-month period in 1947, the loss due to corrosion and damage of engines in ordinary non-metal containers was $4,750,000. But in 1952, over a similar 5-month period, for the same number of engines in steel containers, such loss was reduced to a mere $1,750.

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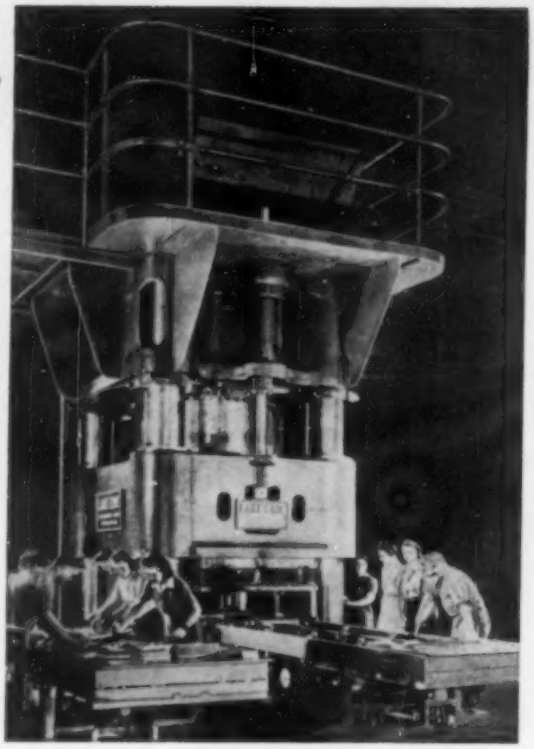

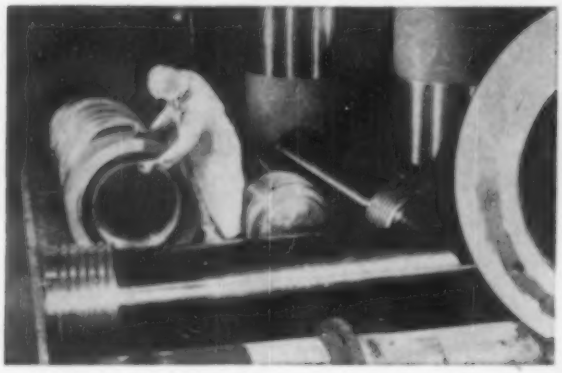

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American Standards Assn. notes that U.S. business now uses 1440 standards. One of the most important standards of the 64 new standards and 88 revisions approved last year was for transformers. It is expected to save about $100 million within the next three years.

Use of liquid uranium in a nuclear power plant to generate electricity is being studied by a group of 14 firms and three organizations of the Atomic Energy Commission. Brookhaven National Laboratory, Upton, N. Y., started preliminary work recently. Babcock & Wilcox Co. heads the study.

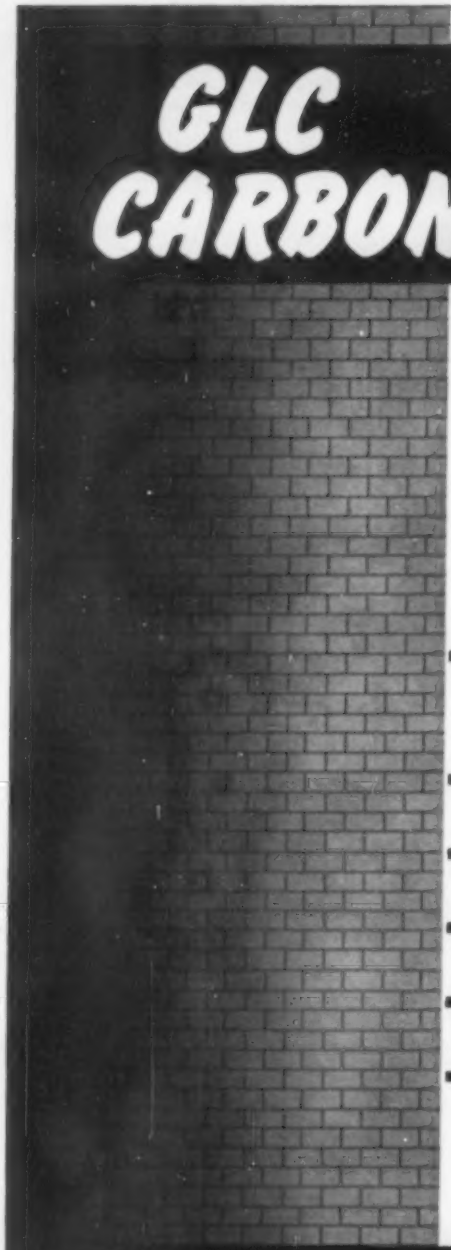
Domestic production of commercially pure titanium sponge metal during 1954 reached an estimated 5300 short tons, more than double the 1953 output of 2241 tons. Titanium sponge purchased by the Government last year, under a General Services Administration purchase and resale program, totaled approximately 2500 short tons in December 1954.

Estimated Canadian primary aluminum shipments to the U.S. in 1955 will be close to 225,000 tons, compared to 195,000 tons last year, according to Ward Van Alstyne, president of Aluminium Ltd. Sales, Inc., U.S. distributor for the Aluminium Ltd. group of companies. It also has been announced that a contract for expansion of aluminum smelting facilities at Kitimat, B. C., has been let. The expansion calls for an additional 60,000 tons annual capacity, bringing rated capacity to 151,000 tons.

Cerro de Pasco Corp. has arranged an $8 million, five year loan from the Bank of Manhattan Co., Bankers Trust Co., National City Bank of New York, and J. P. Morgan Co., Inc., to assist in its share of funds expected to be needed for the newly organized Southern Peru Copper Corp. Cerro de Pasco is to own 16 pct of the new firm's capital stock.

The U.S. Government took definite action to improve the domestic copper supply by banning all exports of domestic refined copper for February and March. Scrap copper exports for these two months have been limited to 12,000 tons. A steady gain in Northern Rhodesian production is expected to help the U.S. situation by about May.

Metallurgists at the research laboratories of Westinghouse Electric Corp., are conducting tensile tests on metals at temperatures as low as -452°F. Metal specimens are stressed within a specially designed chamber cooled with liquid helium.



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Titanium Fills Need For Super Material In Aircraft Of the Future

by N. E. Promisel

The XFV-1 fighter plane uses its four-pointed X-shaped tail for a landing gear.

TITANIUM use in aircraft can be justified, possibly with a few exceptions, only where a saving in weight is achieved. Were it not for weight considerations, titanium's virtues as a material of construction, of corrosion resistance (with exceptions), strength at moderately elevated temperatures, absence of magnetic properties, etc. could be obtained more economically in other conventional materials, although, it must be realized, not necessarily in the same combination. Austenitic stainless steels, for example, aside from weight savings, offer about the same virtues. However, they do entail use of critical and strategic materials, which is very important.

But weight savings, or conversely, prevention of weight growth, can by no means be passed over lightly. It is vital to the improvement of aircraft, either in terms of military performance or in terms of commercial payload. Fig. 1 shows how the gross weight of bombers and fighters has necessarily increased as the speed of aircraft has increased over the years. It is interesting to note that although speed has increased at most four-fold since 1930, before which there was even slower progress, the weight has increased from six to twenty-fold, not including the new B-52 airplane which would make this weight increase about forty-fold. This increase is truly alarming since it indicates the tremendous weight penalty that must be paid for an increase in performance. Part of this phenomenal increase in weight is due to the multiplying effect within the airplane itself. For example, 1 lb added to the structure of an airplane or to the accessories or payload it carries may necessitate adding more power plant, more fuel, still more structure, more wing area, etc., to carry that single added pound without sacrifice in performance or reliability. The 1 lb may therefore multiply into 10 lb in the final airplane. Furthermore, if the effect of temperature on materials is considered, it will be apparent that if an airplane is designed strong enough for elevated temperature operation, the extra weight of material will generally be a severe penalty to its operation at lower temperatures, where it will obviously tend to be over-designed and therefore unnecessarily heavy. Thus the great significance and interest in using titanium to save weight, is apparent particularly as operating temperatures increase.

The question can well be raised as to just what this weight saving means in terms of performance. It is obvious, of course, that extra weight demands a penalty in terms of increased cost, increased material requirements and increased complexity. Although performance figures for specific airplanes cannot be discussed at this time, it is conceivable that future aircraft could save, through the use of titanium, a few thousand pounds weight in the smaller planes like fighters and possibly up to 10,000 lb in large bombers and transports. In the case of bombers and transports, this could be equivalent to extra payload. Or it could be used to increase range or maximum altitude or to decrease take-off or landing distance by possibly 10 to 20 pct, which is no mean improvement. Even greater improvements could result in the case of the fighter and, in addition, appreciable increase in the rate of climb. Conversely, the weight saving could be used to shrink the airplane size without sacrifice in performance

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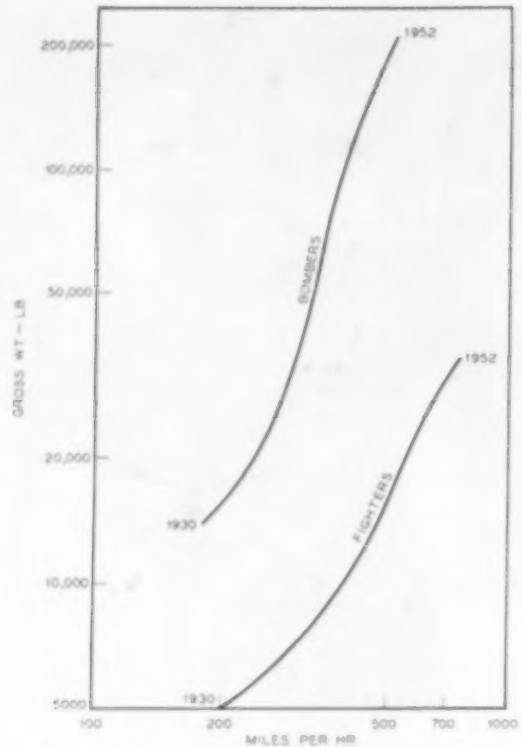


Fig. 1—Airplane growth plotted vs speed demonstrates how the gross weight of bombers and fighters has increased as the speed has increased.

and, under some conditions, the decrease in cost due to smaller size could definitely offset the extra cost due to the use of titanium.

At the present stage of alloy development, weight advantages of titanium over conventional materials show up primarily at elevated temperatures and therefore the majority of current aircraft applications are under these conditions. Elevated temperatures occur in aircraft due to three major causes.

First, materials in the neighborhood of gas turbines, after-burners, heaters, and other heat generating devices increase in temperature in spite of attempts to insulate and cool. Very often space is too limited to permit an efficient insulating job. Furthermore, aside from strength characteristics at elevated temperatures, there is the desire to use a high melting point, high temperature-resisting material as an added precaution so that in the event of failure of a jet or after-burner, flame impingement will not be immediately catastrophic. Unexpected hot spots may also occur.

Secondly, the surfaces of aircraft tend to increase in temperature as the airplanes go beyond the speed of sound, due to aerodynamic heating. The particular temperatures reached depend on many factors such as thermal properties of the surface materials, exposure time and altitude, but Fig. 2 illustrates the approximate magnitude of this effect over a range of altitude from 30,000 to 50,000 ft. Recently, an airplane was flown at a speed over 1600 mph. Were this speed maintained for a long enough period, it could correspond to a temperature of about 400°F, which is often getting beyond the range of efficient use of aluminum and magnesium.

The third major cause of elevated temperatures in airplanes is due to the fact that some parts of airframes and engines necessarily function at elevated temperatures; for example, areas heated for de-icing purposes, vents and tubing for conducting hot air, the compressor, and other parts of jet engines.

Now it is important to realize that in most of the cases of elevated temperature very high stresses must also be considered. In fact, as speeds go higher, wings tend to get thinner, space becomes very critical and stresses go still higher. Temperature gradients may induce high thermal stresses. It is necessary, therefore, to compare the strength of titanium with other structural materials at different temperatures. This is by no means simple because different material properties are involved in different applications. Well over 150 possible detailed characteristics have been counted that might be considered. Only a very few can be considered here.

Strength Characteristics

Gerard[1] of New York University has used two parameters in comparing materials. They are: A—The ratio of density to ultimate tensile strength which serves as a measure of relative weight in tensile applications, and this will be called minimum weight in tension, W_t; and B—The expression:

$$W_{s.c} = \rho \left(\frac{0.002}{\sigma_{cy}} + \frac{1}{E} \right)^{1/2},$$

where σ_{cy} is the compressive yield, ρ is the density, and E is the modulus of elasticity. The expression serves as a measure of relative weight in shear applications and in compression where buckling of plate is critical, and this will be called minimum weight in shear and compression. This type of consideration does not apply to the case where dimensions are fixed and therefore does not include such applications as shear fasteners discussed later.

It should be emphasized at this stage that the curves which follow, not only for the above parameters but for the others in this discussion, should not be taken too literally. High temperature data are extremely sparse and often mutually conflicting, and many approximations, interpolations, and extrapolations were necessary to obtain even these curves. Had time and data permitted, other alloys might have been chosen, some perhaps more favorable to their own material class than in these illustrations. However, the objective in this paper is not to present precise design data, and the conclusions

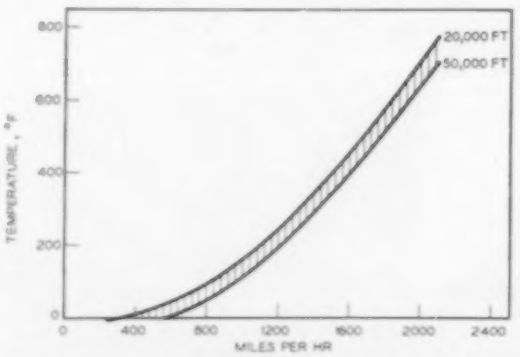


Fig. 2—Skin temperature plotted against speed of flight shows the effect of aerodynamic heating.

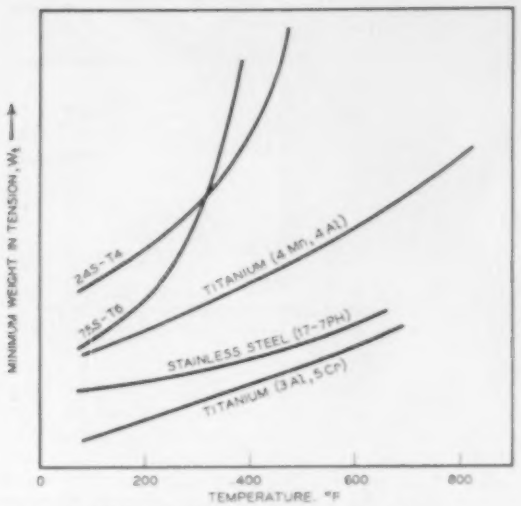


Fig. 3—Minimum weight in tension at various temperatures for some of the high strength aluminum, titanium, and steel alloys of established composition.

reached, as will be seen later, are not dependent on the exact shape or location of these curves.

Fig. 3 shows the relation between W, vs temperature for some of the highest strength aluminum, titanium, and steel alloys of established composition. For simplicity, magnesium alloys have been omitted although under some conditions they have weight advantage over aluminum alloys. Fig. 4 shows this temperature relationship for $W_{s,c}$. The following trends may be deduced from these curves and from other data which could not be included in this paper:

A—In tensile applications, 75S-T6 aluminum alloy corresponds to about the best production titanium *sheet* alloy up to a temperature somewhere near 250° to 300°F. However, precipitation hardened stainless steel, and presumably other steels heat-treated to over about 260,000 psi ultimate tensile strength, would show up to even greater advantage where they could be used as sheet. Above about 300°F, titanium and these very high strength steels are in a class by themselves, with the advantage being toward the steel as the temperature increases. A current experimental titanium sheet alloy is competitive, however, with the aluminum even down to room temperature. Although not shown herein, artificially-aged 24S is superior to 75S-T6 above about 250°F but does not alter the above general trends.

B—In tensile applications for other than sheet, notably forgings, sufficient strength has been developed in titanium alloys to make them appear superior at all temperatures to aluminum alloys, and to be competitive even with super high strength steels.

C—In compression plate applications where buckling is critical and, under some conditions, in shear, the picture may be quite different. Under these conditions, steel appears to be of dubious merit at all temperatures and aluminum has the advantage even at moderately high temperatures, possibly up to 500° or 600°F. It will be noted that in this formula, density and modulus play a more important role than yield strength.

Creep Strength

Creep will be considered simply as the total stretch of the assembly under sustained load. Extensive data on alloys under a variety of conditions are not available but it is quite clear that up to temperatures of a few hundred degrees the creep properties of titanium, both unalloyed and alloyed, tend to be substantially inferior to the yield strength. After that, there is a tendency for creep to follow yield more closely until the upper part of the useful high temperature range, at which stage creep strength drops more rapidly than yield strength. Fig. 5 illustrates this type of behavior, using the 8 pct Mn alloy as an example. Obviously, the curves will vary with alloy, time under load, end point selected for creep, etc. Because high-stressed titanium plays its most important role at elevated temperatures, and because a design adequate for elevated temperature is generally more than adequate for room temperature, the current and anticipated trend in design is to use yield strength as the controlling criterion at lower temperatures and creep strength at higher temperatures. Some place this break at about 500° to 600°F. Although values cannot be pin-pointed at this time, it is quite clear that creep strength will be an extremely important, if not the controlling, factor where sustained high stresses at elevated temperatures are involved. Certainly in gas turbine compressors, creep is of vital importance. Although graphs comparing aluminum and titanium alloys in creep above 400° or 500°F are not presented, it can be stated that on a weight basis, the titanium alloys are superior.

Some comparative data prepared on creep-rupture properties on an *equal weight* basis is available.

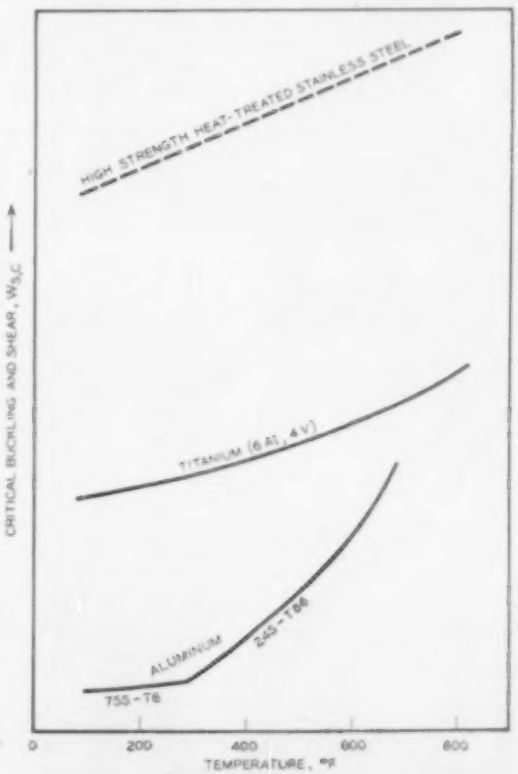


Fig. 4—Temperature relationship for critical buckling and shear, $W_{s,c}$, for some high strength aluminum, titanium, and steel alloys.

In Fig. 6 it is evident that the strength of titanium in this respect is superior to aluminum even at 400°F in less than 10 hr life. At about 1000°F, which is really above the usual temperature of titanium, it is still competitive with stainless steel until almost 1000 hr life under stress.

In Fig. 7, there are plotted curves for the highest strength production aluminum alloy, XA78S-T6, the titanium alloy RC130B and a stainless steel heat-treated to well over 200,000 psi.[6] It will be seen that up to about 300°F, the aluminum and titanium are competitive and superior to steel, and above that temperature range titanium and steel are competitive with each other and superior to the aluminum.

It is possible to go on and on with these comparisons. For example, fatigue properties have not been discussed which are essential in compressor blade applications, or the effect of extended elevated temperature operation on room temperature properties, or relative fabrication properties. But it has been demonstrated that titanium is not a panacea for all structural material problems, even at elevated temperatures, and that there are many places where it should not and will not be used. Only by a careful consideration of each type of application can it be decided if titanium can be used to advantage. On the other hand, it is quite evident that there are many types of application in which no other material could be expected to serve so well.

As indicated previously, titanium has been used mostly in moderate temperature applications to gain experience and uncover future pitfalls, essentially in existing designs as a substitute for steel. Mainly unalloyed titanium has been used for sheet applications, to avoid fabricating and welding problems, and alloys have been used where forgings are concerned. This had led to applications such as firewalls, shroud assemblies, bulkheads, doors, high

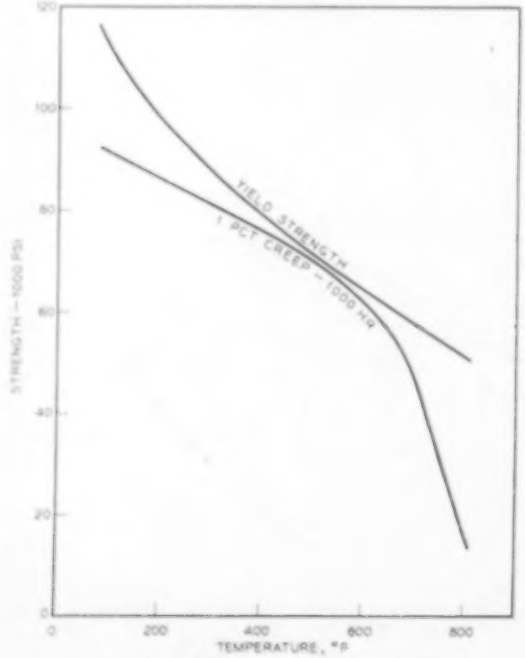


Fig. 5—The relationship between creep and yield properties of titanium is shown using the 8 pct Mn titanium alloy as an example.

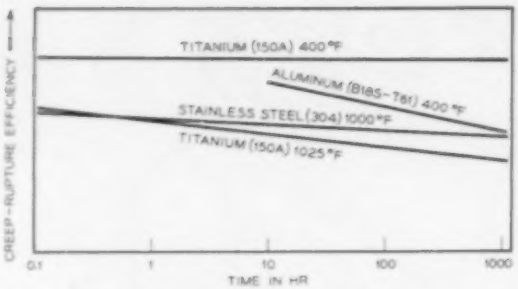


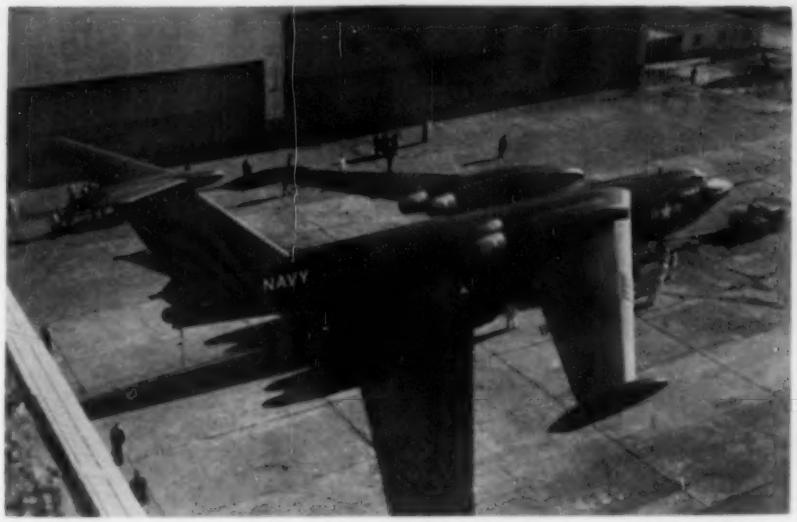
Fig. 6—Comparative data on creep-rupture properties prepared on an equal weight basis is shown for representative alloys.

temperature ducting, engine nacelles, and other sheet applications. Forgings have been the main form of use in jet engines, primarily as compressor disks, compressor blades and as spacer rings. The weight savings, even though significant in many cases, have not been maximum because titanium was not generally planned in the design stage. Other advantages have accrued, however. In addition to fabrication experience and encouraging the infant industry, major hazards have been pin pointed. For example, tests on engine forgings have emphasized how serious can be the effect of hydrogen in impairing ductility. Associated with hydrogen, the importance of alloy selection, rate of strain, duration of load, metallographic phase, notches, etc., have been well brought out by practical trial, thus minimizing possible serious failures in the future. Furthermore, the importance of a thorough understanding of the interdependent role of all interstitials is now well recognized and plans are underway to give this and related subjects accelerated attention, to permit maximum titanium usage, with safety, in the future. A related item is the matter of chemical analysis, for elements are dealt with which are inherently difficult to analyze in minute concentrations.

Supply and Requirements

Another factor which has often been salient is the matter of supply and requirements. Considerable concern has been expressed by the aircraft industry as to the availability of sponge and mill products, in the proper quality and form, if industry went to an all-out plan for using titanium to the maximum beneficial extent. This concern has been a natural one and has been shared by the military departments in view of the serious set-back to aircraft production which could result if design were based on a material not available when needed. The attempts to expedite growth of this industry and exploit titanium at the earliest practical date, instead of taking a more normal course covering decades, has inevitably led to peaks and valleys and unsynchronized situations in the supply and requirements picture. Gradually, however, these discrepancies are being smoothed out and there is increasing assurance of adequate material, so that designers may depend on its availability with growing confidence. One estimate of availability of sponge and mill products is given in Table I.

Table I does not take into account the recovery of scrap, which is being utilized to an ever-increasing extent. Nevertheless, scrap remains one of the serious problems, a more complete solution to which would aid considerably in lowering the expense of



Huge T-shaped tail towers three stories high above the Martin XP6M-1 Seamaster. Plane carries a crew of five and is powered by four Allison J-71 Turbojet engines.

using titanium and simultaneously would increase availability. It may be said also, in passing, that attention is being given to melting and fabricating facilities to balance with raw material availability.

Looking ahead with respect to potential requirements, it is, of course, not possible for a number of reasons to give at this time anything like precise figures. It is possible, however, to indicate the magnitude of these figures. For security reasons, the figures used here are based on those appearing in public documents and are not necessarily figures used or adopted by the Dept. of Defense. Current announced thinking points to reaching full aerial strength and almost complete modernization of military aircraft by the end of 1956 or the middle of 1957. Thereafter, somewhat more than 6000 planes will be needed annually for replacement and continued modernization. Assuming that this corresponds to roughly 250 million lb of combined airframe and engine weight. On the basis of some industry estimates that one third airframe structural weight and about 10 to 20 pct engine weight might advantageously be titanium in the future, the above aircraft weights could correspond to 30,000 tons of titanium sponge. If to this are added factors for spare parts and conversion from raw material and mill products to finished form, in which the losses are currently considerable, the total could well become 3 to 4 times the above figure. In a sense, these are extremely conservative, but again it is emphasized that there are a number of *ifs* in this program which could change the values very radically indeed and these figures should not be used or quoted out of context. It is evident, however, that the potential requirements for titanium, after less than a decade from its introduction as a laboratory material, place the titanium industry as a potential runner-up (in tonnage) of the magnesium industry and approaching something like half that part of the aluminum industry devoted to aircraft. This is extremely impressive and represents again what the teamwork of producers, consumers, and government, supported, of course, by many millions of dollars, can accomplish.

Table I. Estimate of Availability of Titanium Sponge and Mill Products, Tons

Product	1954	1955	1956	1957
Sponge	2200	7700	20,000	20,000
Mill Product	2000	4000	12,000	21,000

Of the titanium requirements, by far the most are expected to be in alloy form, possibly as much as 90 pct. It is expected that all the various forms of wrought material will be used; sheet, plate, extrusions, forgings, and tubing. Although sheet is the most common form now used, there is a good likelihood that forgings will begin to predominate, due to jet engine usage. Need for forgings up to 2000 lb and plate up to 9000 lb has been envisioned. The role of castings is not so clear though definite progress has been made.

Although no attempt is being made in this discussion to cover all future uses of titanium, the subject cannot be left without brief reference to titanium fasteners. Very gratifying progress has been made in high strength bolts and special fasteners directly interchangeable with those of steel and therefore offering about a 40 pct saving in weight. These fasteners are already scheduled for use in production of naval aircraft. Shear applications are of first major interest, with current values of shear strength at about 100,000 psi but expected to approach 150,000 psi eventually. As an illustration of weight savings achieved purely on a fastener substitution basis, in the case of fighter type, it is expected that 200 to 300 lb will be saved. In the case of a bomber or transport size, savings can amount to about 1000 lb.

Any extensive tonnage use of titanium in the near future for guide missiles is unlikely except possibly for fuel tanks. In the more distant future their picture is expected to be quite different.

Conclusions

The major factors and areas determining future use of titanium can be summarized as follows: A—Titanium offers one of the brightest hopes for minimizing aircraft weight and size as airplane speeds plunge deeper into the supersonic range (above 1000 mph) and operating temperatures and times increase (temperatures just a few hundred degrees higher). Under some conditions, particularly certain conditions of compression and stiffness, the high strength aluminum alloys are superior at low tem-

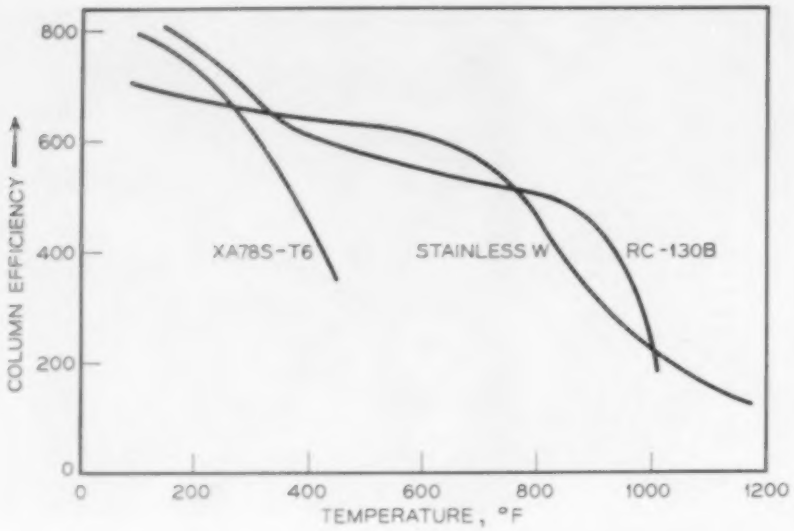


Fig. 7—Strength curves are shown based on data compiled by the National Advisory Committee for Aeronautics[2] on column buckling efficiency, high loads, or short columns.

peratures, and some heat-treated stainless steels are superior at high temperatures, and low alloy steels heat-treated to about 275,000 psi also give competition. The most general structural advantage of titanium shows up above about 300°F.

B—Specialized corrosion applications, such as guided missile fuel tanks, and the need for light weight, high strength, nonmagnetic material in special applications will also dictate use of this material. Increasing need for conserving space in high speed aircraft is an additional influence toward greater usage.

C—Subject to improvement in certain properties to be described, usage will expand to cover forgings (which may well predominate in tonnage), sheet, plate, extrusions, tubing and, to a more limited extent, castings. Future uses of titanium alloys will keep pace with advancements in alloy properties and fabricability including welding. For example, with alloys of improved formability will come increased usage in certain high strength skin assemblies. We may also look for increased use of forgings in important structural attachment points in airframes. Other potential new uses include titanium alloy propellers, landing gear components, armor, plumbing (tubing and fittings), fasteners, and an increased number of jet engine compressor components, as temperatures keep steadily rising. Also possible is a sandwich type construction using titanium skin. Uses in auxiliary equipment should increase steadily.

Some aspects of the current deficiencies in titanium and the direction of future emphasis to permit maximum expansion of usage are:

A—Uniformity and reliability of quality must be emphasized.

B—Cost must be reduced.

C—To overcome deficiencies in certain compression and stiffness applications, alloys must be developed with higher modulus and/or lower density.

D—Stability at elevated temperatures and ability to resist sustained static and vibratory loads, in notched condition, at elevated temperatures (at least 500° to 1000°F) must be enhanced. Oxidation resistance must be improved or protective coatings developed for usage much over 1000° to 1200°F. The physical metallurgy and physical chemistry of the alloys and their behavior under the above conditions must be understood and be predictable, particularly with respect to the interdependent role of interstitials.

E—A formable, preferably weldable, sheet alloy in the order of 175,000 psi ultimate tensile strength should be made available. Forgings and extrusions should be even stronger. Ductility is important.

F—High strength alloys, particularly forgings, good up to at least 1200°F and with adequate oxidation resistance, should be developed.

G—More data must be generated on a variety of elevated temperature properties.

H—There must be reduced production of scrap and greater reuse of it.

Current plans look toward annual production of possibly 25,000 to 35,000 tons of sponge in 1957 with reuse of scrap increasing this figure significantly. The *potential* requirements in aircraft alone, beginning about that time, could easily exceed that figure many times bringing the titanium industry into the magnitude of the present magnesium industry. It should be noted, however, that present production requirements and confirmed future requirements, thus far, do not encourage the above potential figures. To what extent the latter are approached in the next few years depends on the degree to which present practical, and perhaps additional psychological, difficulties and deterrents are removed.

One fact cannot be over emphasized, the stage has been reached where in extremely efficient and advanced military equipment, such as aircraft of the future, design and performance will be limited specifically by material deficiencies. Titanium offers one very bright prospect for partially filling this need for super materials.

References

[1] George Gerard: Life Expectancy of Aircraft Under Elevated Temperature Conditions. *Technical Report 53-493* (October 1953) New York University.

[2] G. J. Heimerl and P. J. Hughes: Structural Efficiencies of Various Aluminum, Titanium, and Steel Alloys at Elevated Temperatures. *Technical Note 2975* (July 1953) National Advisory Committee for Aeronautics.

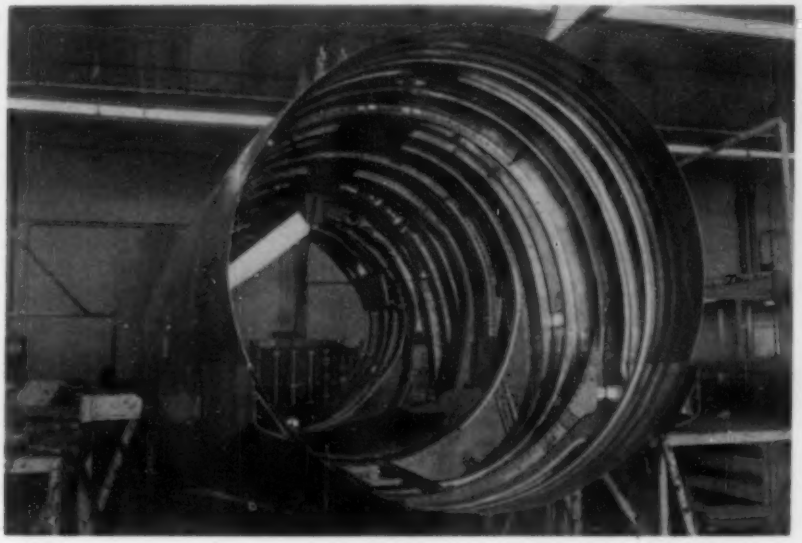


Fig. 1—Aft fuselage of current fighter plane is manufactured almost entirely of titanium.

North American Aviation Inc. Expands Use of Titanium to Airframes

by Gorden Fairbairn

INITIAL use of titanium in the engine nacelles of the X-A2J airplane resulted in a weight saving of approximately 120 lb per ship. The parts were formed on power brakes, hydropresses, and drop hammers. From this beginning, the use of titanium at North American has expanded to include titanium alloy sheet, bar, and forgings to the extent that the aft fuselage of a current fighter airplane in production is manufactured almost entirely from titanium as shown in Fig. 1.

There are two main reasons why titanium is attractive to the aircraft designer as an engineering material: A—Titanium has a favorable strength to weight ratio when compared to other commonly used metals; and B—Titanium has excellent corrosion resistance in media common to aircraft service conditions. This combination of high strength, low density, and excellent corrosion resistance is a boon to the aircraft designer. An added bonus in the titanium picture is the elevated temperature strength of titanium which retains its usefulness at temperatures up to approximately 700°F. This property comes at a very opportune time for aircraft designers of high speed jet airplanes. In such airplanes, the designer is faced with higher and higher service temperatures for the airframe structure. The high strength aluminum alloys such as 24S-T3 and 75S-T6 are no longer useful at the higher temperatures. At 250°F the strength of 75S-T6, the best aluminum alloy, begins to fall off rapidly. Until the advent of titanium, the only alternative would have been to use stainless steel.

Titanium comes into the picture with approximately equivalent strengths and a 40 pct lower density. For an example, ½ hard stainless steel sheet has as design strength a tensile ultimate strength of 150,000 psi and a tensile yield strength of 110,000 psi. The 8 pct Mn titanium alloy sheet has a design tensile ultimate strength of 120,000 psi and a yield strength of 110,000 psi. Fig. 2 illustrates a comparison of the strength weight ratio of titanium vs some common aircraft materials at temperatures up to 700°F.

Other factors than tensile strength must be considered in design and the magnitude of the weight saving gained by using titanium will vary depending on the application. In consideration of the high cost of titanium (about $20.00 per lb in sheet form) the designer must carefully analyze each potential application for titanium to ascertain whether the weight saved is worth the cost entailed by using titanium. Titanium has a relatively high shear ultimate strength and tensile yield strength in relation to its tensile ultimate strength. This means that titanium generally has a weight saving advantage

G. FAIRBAIRN is Supervisor, Engineering Material and Process Group, North American Aviation, Inc., International Airport, Los Angeles. This paper was presented at the AIME Institute of Metals Div. meeting, Chicago, Nov. 1 to 3, 1954.

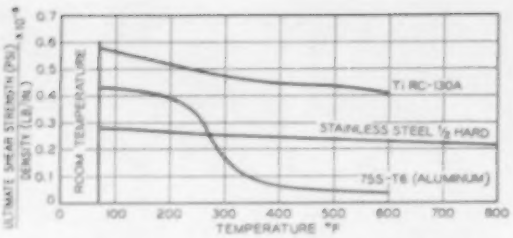


Fig. 2—Strength weight ratio of titanium is compared with some common aircraft materials at various temperatures.

over stainless steel for shear application such as fuselage skins and shear webs. On the other hand, in applications involving plate buckling such as upper wing skins, titanium will not usually save the designer any weight. Here the lower compression modulus of titanium (15 million psi) results in an unfavorable strength weight ratio as compared to stainless steel having a compression modulus of 26 million psi. Other factors such as minimum gage thickness must be considered. For example, a particular design may be satisfactory from a structural analysis standpoint if made from 0.018 gage stainless steel sheet but practical considerations such as part handling may limit the sheet thickness to 0.025 gage. At this gage thickness titanium may be structurally satisfactory, and a weight saving can be realized in direct proportion to the density ratio of the two materials.

At the present time applications of titanium at North American Aviation have been mainly in commercially pure sheet and the 8 pct Mn alloy sheet. The design properties for these materials are shown in Table I. The commercially pure titanium sheet is used mainly for nonstructural applications such as shrouds, firewalls, and air ducts. The alloy sheet is used for structural applications such as skins, frames, longerons, and shear webs. The emphasis has been on sheet materials because it is here that the major weight savings can be realized. In the case of bar and forgings, the currently used low alloy steels, in the higher heat treat ranges can generally compete favorably with the current commercial titanium alloys on a strength weight ratio basis. New higher strength titanium alloys are under development which would conceivably alter this picture. Titanium extrusions, testings, and fasteners also have a potential usage for aircraft applications.

Table I. Comparative Properties of Sheet Materials at Room Temperature

Data	75S-T6 Clad Aluminum	½ Hard Stainless Steel	Titanium 8 Pct Mn Alloy	Titanium Commercial-Pure
Ultimate Tensile Strength, psi	74,000	150,000	120,000	80,000
Yield Tensile Strength, psi	65,000	110,000	110,000	70,000
Yield Compressive Strength, psi	66,000	85,000	110,000	70,000
Ultimate Shear Strength, psi	44,000	80,000	100,000	77,000
Ultimate Bearing Strength (e/D = 2.0), psi	141,000	263,000	260,000	180,000
Yield Bearing Strength (e/D = 2.0), psi	104,000	175,000	175,000	112,000
Modulus of Elasticity in Tension, psi	10.3×10^6	26×10^6	15.5×10^6	15×10^6
Modulus of Elasticity in Compression, psi	10.5×10^6	26×10^6	15.5×10^6	15×10^6
Density, lb per cu in.	0.101	0.280	0.171	0.163

Fabrication Characteristics

Discussion will be limited to commercially pure sheet of the 80,000 psi tensile strength grade and the 8 pct manganese alloy sheet (120,000 psi tensile strength). Titanium is not an easy material to work with in fabricating sheet metal parts. The main reasons for this are: A—Inconsistency in material properties which result in springback variations on die formed parts, premature necking on stretch forming, and localized cracking in many types of forming; B—The inherent characteristics of titanium such as high yield strength, low ductility at room temperature, sensitivity to rate of strain, low uniform elongation, and notch sensitivity; and C—The lack of *know-how* in fabrication techniques applicable to titanium. Some general recommendations for fabricating titanium may be stated. The commercially pure titanium sheet has formability roughly corresponding to ¼ hard stainless steel. The 8 pct Mn alloy sheet may be compared to ½ hard or ¾ hard stainless steel.

Hot forming 500° to 600°F for the commercially pure sheet and 800° to 1000°F for the alloy sheet, may be used to advantage in obtaining tighter bend radii, greater elongation, and less springback or die forming. Hot forming also tends to compensate for material inconsistencies. Slow rates of forming are preferable in order to obtain low yield strengths and greater elongation. Careful edge preparation and elimination of notches is desirable in order to avoid premature failures in forming due to the notch sensitivity of titanium. Finally, it is recommended that titanium be stress relieved following forming operations. At North American Aviation all formed titanium parts are stress relieved at 900° to 1050°F. Stress relieving is necessary in order to prevent delayed cracking due to residual forming stresses. Stress relieving at 900° to 1050°F also restores the loss in compression properties due to stretch forming. Up to a 20 pct loss in compressive yield strength and crippling strength has been observed after stretch forming.

Material Preparation

Commercially pure and alloy titanium sheet can be pierced, blanked, nibbled, friction sawed, and sheared using a flat bed shear. Edge cracking is a

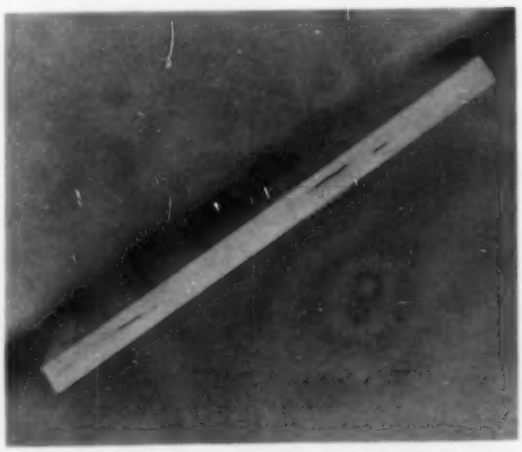


Fig. 3—Edge cracking is a problem in all operations except sawing. Edge cracking as experienced on shearing titanium sheet is illustrated.

Fig. 4—Small titanium parts are formed in a hydropress. One disadvantage of this press is the small working area of the press relative to its overall size.

problem in all operations mentioned except sawing. Fig. 3 illustrates the type of edge cracking experienced on shearing. Sharp tools, close blade clearances and the use of heat will minimize the edge cracking. In severe cases of cracking, filing and sanding of the cut edges may be necessary in order to remove the edge cracks. Edge condition is an important consideration in subsequent forming operations. Deburring is recommended on all cut edges.

Bending

Minimum bend radii of 3t for sheet up to 0.070 in. thick and 3-½t for sheets over 0.070 in. thick have been employed for both commercially pure and alloy titanium sheet. Usual practice is to recommend to the designers that 4t or larger bend radii be utilized wherever possible in order to avoid cracking due to inconsistent material. Hot bending at temperatures of 500° to 600°F for the commercially pure and 800° to 1000°F for the alloy is generally recommended for long bends and for material over 0.050 in. gage thickness. Bending of production parts at North American Aviation is usually done with conventional power brakes using standard male blade punches and female channel dies. A nominal channel width of 4R + 2t (where R is the bend or punch radius and t is the nominal sheet thickness) is commonly used.

Press Forming

Slow forming rates have been found preferable for titanium. For this reason the hydraulic type press has proven more successful than the mechanical crank type. Heat is generally employed for die forming operations at North American Aviation. Standard practice is to heat the blank to the desired forming temperature and form the part on an unheated die. Dies are sometimes heated to approximately 300°F in order to avoid a chilling effect on the hot blank.

On hydropress rubber forming, special heat resistant rubber pads are used. Chopped asbestos has also been utilized to insulate the rubber from the hot blanks. Fig. 4 illustrates some small titanium parts being formed in a hydropress. Hydraulic-forming machines which provide high uniform unit pressures on all areas of the blank being formed have proven very successful for forming difficult parts at room temperature. A disadvantage of this type of press is that the working area is rather small in comparison to the overall size of the press.

Drop Hammer

Drop hammer forming is used extensively at North American Aviation for parts having complex contours. Originally, drop hammer forming was not considered suitable for titanium because of the desirability of forming titanium slowly. This has been overcome by doing all drop hammer forming on blanks which are heated to 1050°F prior to forming. This technique has produced very satisfactory results on drop hammered parts. In fact the scrap rate due to material failures in forming has been generally lower on drop hammers than with other types of forming. Die materials are a problem due to the use of heated blanks. Kirksite, which has commonly been used for drop hammer dies is not satisfactory for hot forming titanium where large volumes of parts are involved. Die dimensions tend to get out of tolerance due to the softening of the die in contact with the heated blanks.

Other die materials have been investigated, such as ductile iron and steel, and have proven satisfactory. The main disadvantage in using drop hammer

Fig. 5—A finished titanium part is shown on a drop hammer die. Drop hammer forming produces a larger ratio of blank weight to finished part weight than other types of forming.

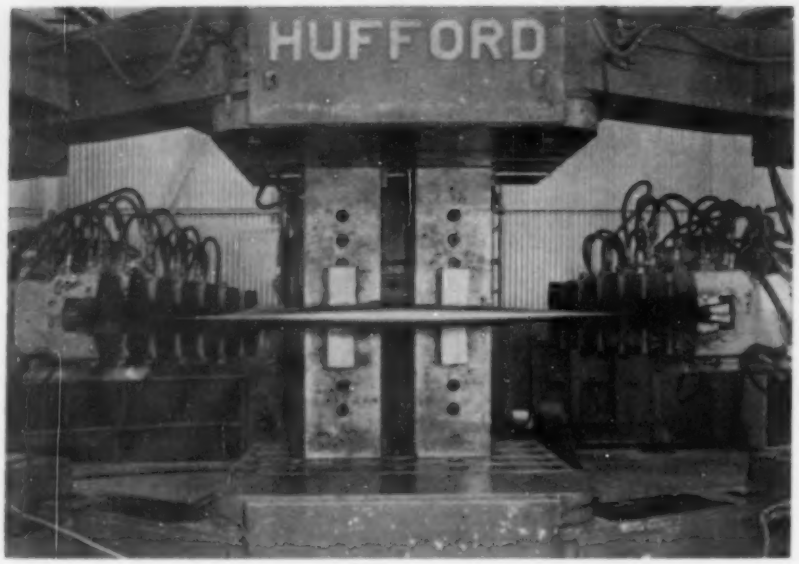


Fig. 6—A wing tip is shown being stretch formed. Stretch forming of titanium remains one of the more troublesome operations at North American Aviation.

forming on titanium is that the ratio of blank weight to finished part weight is large as compared to other types of forming. Excess material is needed for traps in order to prevent wrinkling on forming and this material is lost as trim scrap. Fig. 5 shows a finished part on a drop hammer die.

Stretch Forming

Stretch forming is used for contouring fuselage skins and substructure such as frames and longerons. This method of forming titanium is useful for making shrink flanges which are difficult to form without wrinkles on other types of forming equipment. The low uniform elongation, narrow spread between tensile yield and ultimate strength, and inconsistent properties of titanium cause difficulty in stretch forming. Hot forming methods have been tried experimentally but have not proven practical to date. The use of heat tends to produce localized necking due to the difficulty in maintaining uniform temperatures over the blank during the relatively long time required to complete the forming operation. Intermediate anneals at 1050°F between multiple forming stages has reduced the scrap rate and resulted in more consistent contours. Stretch forming of titanium remains one of the more troublesome operations at North American Aviation. Figs. 6 and 7 illustrate respectively a wing tip and fuselage skin being stretch formed.

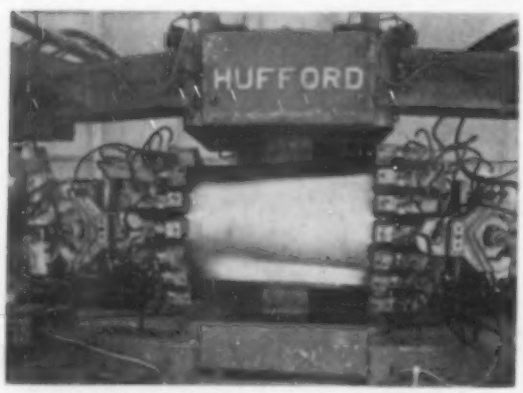


Fig. 7—Contouring fuselage skins is done by stretch forming. Scrap rate has been reduced by intermediate anneals between multiple forming stages.

Joining

Commercially pure titanium and titanium alloy sheet metal parts are assembled at North American by means of riveting using Monel rivets. The commercially pure titanium is also assembled to itself by means of spot and seam welding. For riveting, brazier head rivets are generally used for internal structure, and flush head rivets are used for external skins. In flush riveting, commercially pure and alloy titanium sheet is either machine counter-sunk or coin dimpled depending on the material thickness. Gages less than 0.063 in. are dimpled. For dimpling the pure or alloy sheet, the dimpling dies are heated to 750°F and a dwell time of 6 sec is used to provide sufficient heat in the sheet prior to dimpling.

In spot or seam welding of commercially pure titanium, standard equipment and procedures used for stainless steel are satisfactory. The surface of the titanium sheet must be free from annealing or hot forming oxides prior to welding. A ratio of tensile strength to shear strength of about 0.3 is normal for spot welded commercially pure titanium.

Assembly Techniques

Because of the cracking tendency of titanium and its resistance to local deformation, it is very necessary that proper contours and close fit-up be maintained in assembling titanium parts. If parts do not match, it is better to use shims to take up gaps rather than attempt to force parts together in riveting. A common practice at North American Aviation has been to shim any gap over 0.010 in. rather than close the gap by riveting. This means that details produced by the forming departments should be held to closer tolerances than commonly maintained with other aircraft materials such as stainless steel. Check templates and jigs and assembly fixtures must be carefully checked to insure the proper mating of detail parts. In short, it is necessary to do a better job than previously necessary on common airframe materials while using a new metal on which fabrication techniques are still being developed.

Fig. 1—After completion of brick work, the furnace was cleaned and a wood form erected for regulating the thickness and the shape of the rammed bottom.

Maintenance of Electric Furnace Bottoms As Practiced in Bethlehem Plant

by H. C. Bigge

FURNACES making steels of high alloy content require superior refractories because of the high temperature during meltdown and refining and the special slags used. Difficulties in the hearth caused by slag and metal penetration necessitate the use of high magnesia refractories.

At Bethlehem 96 pct MgO is used for cold ramming a new bottom. Three features are claimed for this material that make it unique in performance compared with other ramming materials. These are:

A—The chemical analysis is what operators have been trying to obtain for years. A typical analysis is 96.67 pct MgO, 1.07 pct CaO, 1.04 pct SiO_2, 1.22 pct R_2O_3 impurities.

B—Its bulk density allows it to ram up to 180 lb per cu ft, which makes it an excellent bottom material, especially in electric furnaces where a great deal of reducing slag is absorbed into the conventional bottom.

C—It has low shrinkage, less than 1.00 pct. The manufacturer claims it does not have to be sintered because it forms its ceramic bond at 1500°F, which eliminates long burning-in time and increases production. It is recommended that the material be cold rammed up to the working surface without any magnesite or foreign material burned over the top. The green crushing strength is 6000 to 9000 and it will stand a hot load of 25 psi to temperature in the range of 3450° to 3540°F. The reversible thermal expansion is approximately 2.3 pct from room temperature to 2550°F.

Within the past three years Bethlehem installed four bottoms of 96 pct MgO, in four different furnaces; one 7-ton furnace, 11-ft diam shell; one 25-ton furnace, 15-ft diam shell and two 50-ton furnaces, 18-ft diam shell. It was found that the material forms a ceramic bond at approximately 1500°F; therefore, it is necessary to provide means for eliminating the moisture from the ramming mix when heating it.

The average furnace bottom and outer shell are so constructed that it is difficult for the moisture to escape, with the result that it accumulates underneath the rammed bottom or the bottom of the brickwork where superheated steam is formed.

To eliminate this condition, vents were provided in the steel shell, consisting of drilled holes of ½-in. diam equally spaced around the vertical center line of the furnace shell. A new steel bottom plate was placed in the furnace and welded to the shell, vent holes and hole for the pyrometer tube were drilled, and six ⅛x2x36-in. conductor strips were welded to the inner shell.

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This is an abstract of a paper presented at the AIME Electric Furnace Steel Conference, Pittsburgh, Dec. 1 to 3, 1954.

Fig. 2—Recommended range of thickness for electric furnace hearth is 6 to 12 in. The ultimate density of the rammed structure will depend upon the thoroughness of the ramming.

A 1½-in. chrome concentrate plastic was rammed on the bottom plate. Two soldier courses of chrome magnesite with 24 pct Cr_2O_3 and 39 pct MgO, measuring 9x4½x3 in. were put in the bottom, laid in herring-bone pattern, dry, using ⅛x2x10 in. wooden strips between each brick. After each course was completed the strips were removed and dry chrome magnesite cement of the same composition as the brick was swept between the brick joints.

Upon completion of the bottom, sidewalls were laid out with a 4½ in. brick width on the first course. Each course was racked back up to the sill line where the wall thickness was 20 in. From this point back-racking with chrome-magnesite brick was continued to the slag line. These brick were all buttered to this point. Balance of the wall was 13½ in. thick to the top of the furnace shell, made with 13½x6x3 in. metal-covered brick, straights and keys with 54 pct MgO and 16 pct Cr_2O_3.

After completion of the brick work, the furnace was cleaned out and a wood form erected as shown in Fig. 1 for regulating the thickness and the shape of the rammed bottom.

For cold installation, the brickwork in the bottom and the side up to about 5 in. above the sill level should be cleaned of dust and brick particles and then scrubbed with an 80 pct sodium-silicate water solution. This prevents the brick from absorbing the moisture from the mixture before it is rammed and set in place.

No more material should be applied than can be properly rammed before it dries out. In large hearths the bottom should be rammed in sections, using wooden forms braced to provide a solid frame against which to ram. On removal of a form, the edge of the mixture next to the form must be well roughened to insure a good bond with the next section.

The mixture should be spread evenly to a depth of 5 in. and ramming started at once, continuing until the thickness is reduced to about 3 in. and a hard surface is obtained. Before each subsequent layer is started, the rammed surface should be thoroughly scored or otherwise loosened with a rake before a layer of loose material is added, to insure a firm bond between the two layers. The ultimate density of the rammed structure will depend upon the thoroughness of the ramming. The recommended range of thickness for an electric furnace hearth is 6 to 12 in., illustrated in Fig. 2.

The most effective type of rammer for compacting the mixture is a floor rammer or backfill tamper with a 3 to 3½-in. diam head. These rammers have a stroke of from 5 to 6 in. and operate efficiently on 80 to 100 lb air pressure.

Rammed bottom of high MgO content, properly installed, have proved more efficient than burned-in bottoms. With a rammed bottom, a hearth high in MgO is obtained without silica (SiO_2) infiltration from overheated walls and roof, as might occur during the process where a bottom is burned-in in layers with electrodes or carbon blocks in T formation.

The rammed bottom, therefore, is more refractory, is easier to build, avoids the time and hazard of burning the side walls and roof and costs no more than the burned-in bottom.

At Bethlehem the coke method as shown in Fig. 3 is used for the burning-in operation. The furnace is filled with clean lump coke (measuring from 2 to 4 in.) level with the door sill. The electrodes are lowered and regulated by hand; high voltage is used for 5 min to ignite the coke directly underneath the electrodes and submerge each electrode approximately 3 in. below the level of the door sill. The power input is then reduced by lowering the voltage and the power is scheduled on the basis of on and off, in order to heat the furnace slowly and uniformly. The use of coke was adopted in 1940 and it is preferred for the following reasons:

A—It maintains a steady contact with the electrodes and gives gradual uniform heating of the flat and banks.

B—It prevents the intense heat of the electric arc from reflecting against areas above the slag line.

C—Coke additions are easy to make.

D—It eliminates difficulty in moving electrodes or carbon blocks when that method is used to burn-in the bottom.

E—It eliminates the difficulty of removing the electrodes from the furnace.

F—After the burning-in operation is completed, about 90 pct of the remaining coke and ash can be removed into a slag pot by tilting the furnace and using a steel rabble or scraper attached to the charging-machine peel. The remainder is absorbed in the wash heat used for completing the installation of the new bottom.

Data on Installation

The 96 pct MgO rammed bottom installed in the 25-ton furnace, 15 ft shell was made as follows: After brick work was completed, the surface of the brick on the bottom and side walls was cleaned and scrubbed with an 80-pct solution of sodium silicate in pure water.

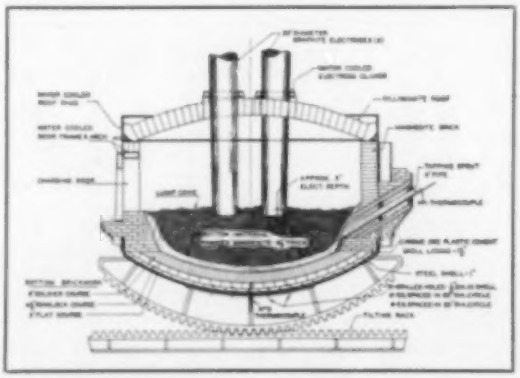

Fig. 3—Section through 50-ton electric arc furnace illustrates coke method for burning-in operation.

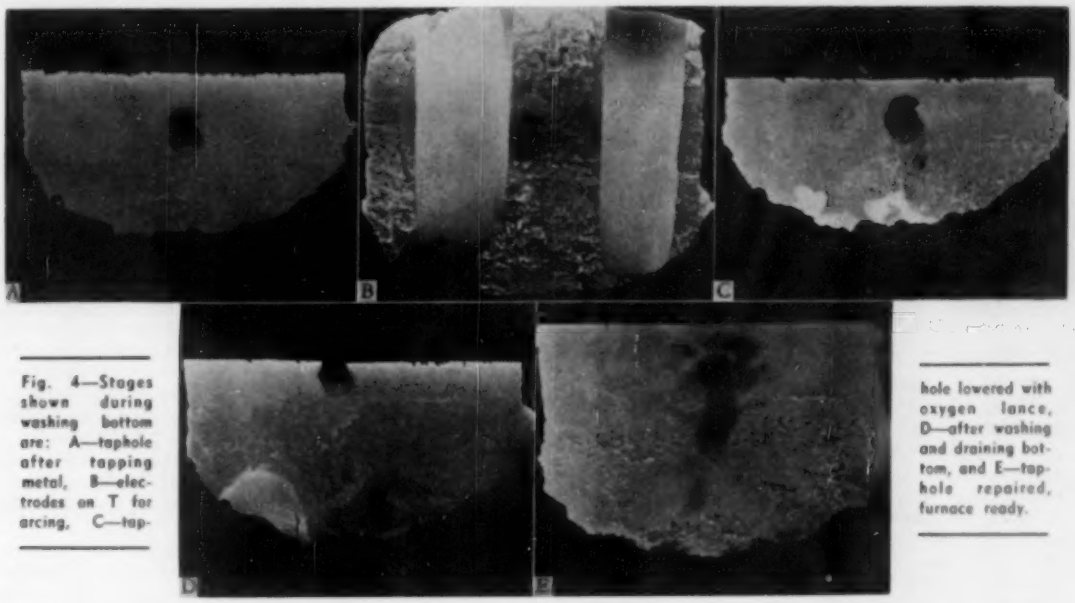

Fig. 4—Stages shown during washing bottom are: A—taphole after tapping metal, B—electrodes on T for arcing, C—taphole lowered with oxygen lance, D—after washing and draining bottom, and E—taphole repaired, furnace ready.

A total of 15,500 lb of 96 pct MgO was used. It was found that 3 pints of water per 100 lb of mixture gave better ramming than larger quantity of water. A total of 58.1 gal or 464.8 lb of water were consumed. The material was mixed in a mechanical mixer in lots of 300 lb. Eight men installed 15,500 lb in 8 hr. After the ramming was completed a charge of 6300 lb of lump coke, size 2 to 4 in., was placed on the hearth to a height even with the door sill, for burning-in the bottom.

The electrodes were then lowered level with the top of the coke, the electrode mast arms were marked with chalk to show their position in relation to the coke, and the power was applied, using hand control. A power of 232 v (5000 amp) was applied for 5 min until the electrodes were immersed approximately 3 in. in the coke bed, and again the mast arms were marked. The power input was then changed to 114 v (5000 amp) and a power input schedule was adopted for the rest of the burning-in operation, representing a cycle of 5 min on and 10 min off. The coke was rabbled with a bar each hour and additions of coke were made during the entire burning-in operation to keep the coke even with the sill level. When necessary, the electrodes were slipped.

A total of 28½ hr was necessary for burning-in the rammed bottom to a hearth temperature of 380°F at 16½ in. below the top of the rammed surface and 180°F on the outside shell of the furnace. The temperature of the side wall above the tap hole was 2700°F, measured with optical pyrometer. The pyrometer tube in the hearth was located in the center of the electrode circle. The outside pyrometer was embedded in the furnace shell, 29 in. from the top of the rammed surface. This double bottom consists of two plates each 1 in. thick, with rammed chrome concentrate between.

The heating schedule was 9½ hr power on and 19 hr power off. The original coke charged weighed 6300 lb, a total of 2725 lb was added during the heating schedule, making a total of 9025 lb to keep the coke at sill level. A total of 16,000 kw hr was consumed during the heating operation. After completing the heating schedule, the furnace was tilted to slag-off position. Steel rabbles were used to rake the coke toward the charging door where it was removed into the slag pot with a mechanical rabble fastened to the charging machine.

It is estimated that approximately 3500 lb of coke were used in the burning-in operation, 5098 lb were removed from the furnace into the slag pot and 427 lb were absorbed in the wash heat which followed immediately after the removal of the coke.

It is important to remove as much as possible of the coke from the bottom before making the wash heat, otherwise difficulty will be experienced in heating the wash heat as the coke will gather on the surface of the molten metal causing excessive heating of walls and roof.

A wash heat was made to remove any excess coke and to set the bottom. The furnace was charged with bundle scrap, power was applied and the scrap melted with a single slag and tapped with black slag.

Maintenance

If difficulty with excessive erosion or a hole in the bank is encountered the 84 pct MgO hot patching material is used up to and including the slag line. Holes must be reasonably clean and should be blown out with air. It must be mixed quite wet (consistency of concrete) for maximum compaction (10 to 12 pints of water per 100-lb sack). This is particularly important in large furnaces or in a location where a patch cannot be reached and tamped in. After patching sufficient time should be allowed for the material to bond, before charging furnace.

Recently difficulty was encountered with excessive erosion of the banks of a 50-ton furnace, making special alloy. After the furnace was tapped, the bottom was cleaned with air and 5000 lb of wet 84 pct MgO was shoveled on the banks. Fifty pct of the scrap charge for the next heat was added and heated slowly for 2 hr. After this charge was about 75 pct melted the balance of the scrap was charged and the banks were satisfactory after making and tapping the metal.

Table I. Analysis of Calcined Dolomite Used for Maintenance and of Furnace Bottom Before Washing, Pct

Material	Calcined Dolomite	Bottom Before Washing
MgO	34.80	33.90
CaO	51.30	46.70
Fe_2O_3	0.80	4.40
FeO	—	8.50
Al_2O_3	0.74	2.50
Cr_2O_3	—	0.04
SiO_2	1.78	11.20
TiO_2	0.02	—
Alkali	0.26	—
Ignition loss	0.70	—
MnO	—	1.42
P_2O_5	—	0.11
SO_3	—	0.052
C	—	0.06

When necessary to hot patch the side walls above the slag line, 65 pct MgO granular refractory is used. When the proper amount of pure water is added and thoroughly stirred, the mixture can be applied to the side wall by shovel; it will adhere well to the vertical walls. The gunmix refractory is used for maintenance of sidewalls on the 11-ft furnace. It is applied with a special gun with a stream of air and water. It has high refractoriness, rapid coalescence with hot surfaces and adheres to vertical walls when applied at high temperature.

Records show that the average number of heats per bottom may vary widely, from 700 to 4400 heats, or from months up to four years. No set rule may be advanced, except that a bottom should be renewed when it becomes difficult to maintain or when it gives trouble with quality of steel produced. At the Bethlehem plant a general rebuild is made after approximately 2000 heats, equivalent to two years continuous operation.

Present 25 and 50-ton furnaces have stationary roofs. Their average production of ingots is 34 net tons for the 25-ton furnace and 62 net tons for each of the 50-ton furnaces.

The nominal depth of the bath is 31 and 35½ in. The tap hole is constructed for the use of a 4 or 5-in. diam pipe, when making the tap hole to restrict the slag and give a tight round tapping stream. The hole is closed with a mixture of calcined dolomite and calcined coke. There are times when it is necessary to produce larger taps, 36 net tons from the 25-ton furnace and 74 net tons from each of the 50-ton furnaces, for the production of larger ingots. This results in a larger slag volume and sometimes causes accumulation of slag. A large variety of alloy and special steels is also made which cause alloy bottom contamination.

To correct this condition, the bottom and banks of each furnace are washed as needed, using 18 to 24-in. lengths of 12, 18, or 20-in. diam electrodes placed on the flat of the furnace with the charging machine and arranged with a peel mounted on the charging machine, for T formation for arcing. Power is applied to heat the flat and bottom, and then mill scale and fluorospar are spread over the banks and flat. Power is again applied and after the metal and slag accumulate on the flat, the tap hole is lowered with an oxygen lance and the furnace is drained.

The banks and flat are repaired with calcined dolomite. Heat is again applied until the bottom is clean, after which the electrodes are removed from the bottom and the tap hole repaired. The electrodes are returned to a higher position in the holders and the bottom is allowed to set 45 min before recharging. A total of 5 hr and 55 min was required for this operation. In the 25-ton furnace it was done in 3 hr. Fig. 4 shows the tap hole during various stages in washing bottom.

The analysis of the calcined dolomite used for maintenance and the analysis of the slag taken from the bottom before washing the furnace are given in Table I.

Since all basic furnace practices include the use of lime-rich slags, even hearths that were originally of high magnesia content show unmistakable trends toward the dolomite composition soon after they are put in service. After a few weeks, the chemical change may penetrate the hearth substantially. After a year or two some hearths attain a dolomite-like composition all the way to the monolithic structure.

Tables II and III give the analysis of a bottom taken from a 7-ton basic arc furnace after making 4392 heats. The samples were taken from the extreme bottom adjacent to the brick work.

Table II. Analysis of Bottom Taken From 7-Ton Basic Arc Furnace, Pct

Material	Original Rammed Bottom	Calcined Dolomite for Maintenance	Bottom After 4392 Heats
MgO	64.30	37.14	28.57
CaO	15.60	32.39	37.94
Fe_2O_3	3.33	8.53	1.02
FeO	—	—	2.49
Al_2O_3	2.40	0.27	2.70
Cr_2O_3	2.48	—	0.36
SiO_2	8.20	0.44	7.90
TiO_2	0.14	—	0.21
Alkali	1.50	—	—
Ignition loss	1.17	—	—
MnO	—	—	0.14
S	—	—	0.54
C	—	—	0.05

Table III. Analysis of Metal Mixed with Bottom Material in 7-Ton Basic Arc Furnace

Element	Pct
Fe	89.10
C	0.91
Mn	0.19
P	0.021
S	0.035
Si	0.46
W	0.48
Ni	0.40
Cr	4.66
Mo	3.75

Conclusion

The use of a 96 pct MgO rammed bottom installed by the coke process, with drilled holes in the shell, makes the most efficient installation to date. Washing of the bottom periodically results in less contamination and produces cleaner steel.

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Chemistry of the Ammonia Pressure Process for Leaching Ni, Cu, and Co from Sherritt Gordon Sulphide Concentrates

by F. A. Forward and V. N. Mackiw

The paper relates to the laboratory and pilot plant studies that have been carried out by Sherritt Gordon Mines Ltd., Metallurgical Research Div., in developing the ammonia pressure leach process for extracting copper, nickel, cobalt, and sulphur from high grade nickel concentrate produced from Lynn Lake ores, and describes in some detail the chemistry of the process.

IT is well known[1-6] that copper, nickel, cobalt, zinc, ferrous iron, and a number of other metals combine with ammonia in aqueous solution to form complex ions of the form $[Me(NH_3)x]^{n+}$. The stability and solubility of these ions depend on the concentration of the metal ion in solution, on the amount of NH_3 present, and on the amount and type of anions present, e.g., OH^-, CO_3^{--}, NO_3^-, Cl^-, SO_4^{--}. If ammonia is partially or completely removed from such solutions, for example by boiling, the soluble ammines tend to decompose and the metals precipitate as basic salts.

These properties of metal ammines have found practical application in the commercial recovery of copper, nickel, and cobalt from a variety of ores. In an operation formerly conducted at Kennecott[6-8] the mill tailing containing 0.80 pct Cu as copper carbonate was leached by percolation with an ammonia-ammonium carbonate solution to dissolve the copper as the ammine. At Calumet and Hecla[6-9] with a mill tailing containing about 0.4 pct Cu as metallic copper, it has been found necessary to aerate the ammonia-ammonium carbonate leach solutions between stages to oxidize the solubilized copper. At Nicaro[10-12] where nickel and cobalt occur as oxides and silicates which are not soluble in ammonia, the ore is heated to decompose silicates and to selectively reduce the nickel and cobalt to metal, leaving the iron as Fe_2O_3, and is then leached with ammonia-ammonium carbonate solution accompanied by aeration to dissolve nickel and cobalt as ammines.

In each of these leaching operations, the anion present is CO_3^{--} and the metals can be precipitated from the leach solution as oxide (copper) or hydroxide and carbonate (nickel and cobalt) by boiling off NH_3 and CO_2, both of which are recycled to treat a subsequent ore charge. The products—oxide, hydroxide, or carbonate—can be treated by conventional smelting, calcining, or electrolytic methods to convert them to refined metals. Thus the procedures mentioned utilize the properties of the ammines to extract copper, nickel, and cobalt from nonsulphide ores and separate them from the leach solutions.

These processes have the advantage that they can be carried out in closed vessels at atmospheric pressure, that the leaching solutions are specific for the desired metals, that the metals can be recovered as relatively pure compounds by the boiling operation, and that the NH_3 and CO_2 can be recycled. Also, as the leach solutions after boiling and filtration are substantially free of metals, NH_3, and CO_2, they can be discarded, thus facilitating the control of the water balance in the leaching circuit.

When, as is the case with Sherritt Gordon concentrates, sulphides are treated with ammonia solution in the presence of oxygen, the leach solution contains SO_4^{--}, and an entirely different set of conditions is encountered. The ammine sulphates (of nickel, for example) are more soluble than the carbonates and can be only partially decomposed by boiling. The SO_4 and NH_3 in the solutions can not be recovered by boiling. Thus, despite the more favorable leaching conditions resulting from high solubility of the ammine sulphates, the recovery of metals, NH_3, and SO_4 from the solutions must be effected by other means.

Sherritt Gordon Nickel Concentrate Treatment

The Ni-Cu-Co flotation concentrate produced at Lynn Lake[13] contains 12 to 16 pct Ni, 1 to 2 pct Cu, 0.2 to 0.5 pct Co, 33 to 40 pct Fe, 28 to 34 pct S, 8 to 20 pct insoluble, and less than 0.02 oz per ton precious metals.

The nickel is present chiefly as pentlandite, the copper as chalcopyrite, and the iron as pyrrhotite and pyrite. Most of the cobalt is thought to be present in pentlandite, although it is known that a small amount occurs as Co-Ni-pyrite.

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In considering the applicability of ammonia leach methods for treating material of this composition, the first thought would be that, in view of the difficulty of recovering the metals when sulphate ions are present in the leach solution, the logical procedure would be to roast the concentrate to remove sulphur, reduce copper, nickel, and cobalt selectively in the calcine following in some measure the methods at Nicaro, leach with ammonia-ammonium carbonate solution, separate the copper by cementation, and precipitate Ni-Co hydroxide (and carbonate) by boiling. This procedure was examined[4] and found to work satisfactorily insofar as metal extraction was concerned, but the large number of operations and expected difficulties of plant control suggested that it would not be commercially attractive.

In the course of laboratory investigations, it was discovered that the sulphide concentrate could be dissolved directly in an aqueous solution of ammonia in the presence of oxygen, providing the following chemical and physical conditions were maintained: 1—that sufficient oxygen be supplied in solution to react with the sulphides present in the concentrate; 2—that sufficient NH_3 be supplied to neutralize the acid formed by oxidation of the sulphides; 3—that there be in addition sufficient NH_3 in the solution to form the higher ammines of copper, nickel, and cobalt together with the amount of "unbound" NH_3 necessary to establish equilibrium with the ammines; 4—that there be sufficient anions, SO_4^{--}, etc., present; 5—that the "unbound" NH_3 be not so high as to reduce the solubility of the ammines; and 6—that the temperature be such that the reactions proceed at an acceptably high rate, but not so high as to cause precipitation of basic salts or insoluble complex ammines.

Laboratory and plant studies showed that these requirements could be met by mixing the sulphide concentrate with strong aqueous ammonia solution and leaching at a temperature between 160° and 190°F with vigorous agitation in a closed vessel with compressed air to provide a partial pressure of oxygen of about 10 psi. Under these conditions the iron in the copper, nickel, and cobalt minerals is oxidized and forms hydrated ferric oxide which, together with the silicates, is insoluble in the ammonia solution. The copper, nickel, and cobalt are converted to ammines and the sulphides oxidized to sulphates, thiosulphates and polythionates.

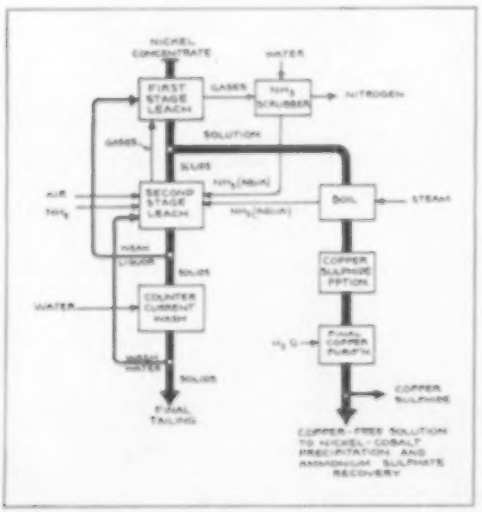

Fig. 1—Flow diagram of leaching and copper-removal circuits.

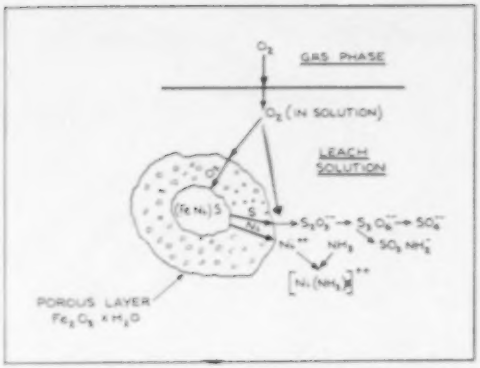

Fig. 2—Diagrammatic representation of leaching sulphide particle (pentlandite).

As the presence in the leach solution of sulphate, thiosulphate, and other ions preclude the possibility of precipitating the metals as oxides or hydroxides by boiling off the ammonia, other methods must be adopted. The precipitation of nickel ammonium sulphate with sulphuric acid[4] is an effective method of separating the nickel from both copper and cobalt. A second method[4] comprises separating the copper quantitatively from nickel and cobalt by boiling the leach solution to drive off part of the NH_3, thus promoting the decomposition of thiosulphate and precipitating the copper as sulphide. Nickel and cobalt can be recovered separately from the resulting copper-free solution[5] by a hydrogen precipitation method developed by Chemical Construction Corp. and Sherritt Gordon engineering and research staffs. The final products from this operation are copper sulphide, nickel metal, cobalt metal, and ammonium sulphate.

It is the purpose of this paper to outline the chemistry of the leaching and copper precipitation operations and to discuss the effect of some of the variables such as temperature, pressure, and ammonia concentration on the reactions involved.

Flow Diagram

Reference to the flow diagram (Fig. 1) will show that the leaching process comprises essentially a two-stage counter-current leach in which pregnant liquor is produced in the first stage. The solids from the first stage are mixed with wash water (containing ammonia) and leaching continued in the second stage. When leaching is complete the pulp is thickened, the solids filtered, washed, repulped and rewashed twice, and discarded. The liquor is mixed with fresh concentrate and charged to the first stage. The exit gases are washed to recover ammonia.

The pregnant liquor is boiled in a continuous unit to recover NH_3, is heated to precipitate copper sulphide, and treated finally with a small amount of H_2S to remove the last traces of copper.

Reactions in Leaching

The leaching action in its simplest form may be described as a reaction between the sulphide minerals in the concentrate, dissolved oxygen, ammonia, and water, in which copper, nickel, and cobalt are converted to ammines, sulphur is converted to an oxidized form, and iron is converted to hydrated ferric oxide. These reactions might be expected to

be influenced in the normal manner by variations in temperature, pressure, and concentrations of ions and of "unbound" ammonia in the leach solution.

There are, however, a number of other factors that serve to complicate the procedure. In the first place, the concentrate contains at least four sulphide minerals—pentlandite (NiFe)S, chalcopyrite ($CuFeS_2$), pyrrhotite (Fe_nS_{n+1}), and pyrite (FeS_2). There is some evidence to suggest that the pentlandite, chalcopyrite, and pyrrhotite react with oxygen, water, and ammonia, to produce soluble salts in such a way that the iron present in each mineral particle is converted to hydrated iron oxide *in situ* with the result that the particles, when leaching is complete, consist of hydrated iron oxide pseudomorphic with the original mineral. If this hypothesis is correct, it could be assumed that, at any given time during the progress of the leach, the leaching particle as represented in Fig. 2 consists of a sulphide core surrounded by an iron oxide envelope through which (in the case of pentlandite, for example) the nickel and sulphur ions diffuse outward to react with oxygen at the liquid-solid interface while the oxygen diffuses inward, possibly by a mechanism associated with vacancies in the oxide lattice. Pyrite does not react measurably under the conditions normally used in leaching: it remains unaltered in the leach residue and any cobalt or nickel in the pyrite can not be dissolved during leaching.

A further complication is that the sulphur in the sulphides is not converted in a single step to sulphate but follows through a series of reactions in which the first product is thiosulpate, this being further oxidized to thionates, which in turn are oxidized to sulphate and sulphamate.

Studies of the leaching action carried out under a variety of conditions suggest that the following reactions take place in sequence, although at any given point in time all are in progress simultaneously

$$NiS{:}FeS + 3FeS + 7O_2 + 10NH_3 + 4H_2O \rightarrow Ni(NH_3)_2SO_4 + 2Fe_2O_3 \cdot H_2O + 2(NH_4)_2S_2O_3 \quad [1]$$

$$2(NH_4)_2S_2O_3 + 2O_2 \rightarrow (NH_4)_2S_3O_6 + (NH_4)_2SO_4 \quad [2]$$

$$(NH_4)_2S_2O_6 + 2O_2 + 4NH_3 + H_2O \rightarrow NH_4 \cdot SO_3 \cdot NH_2 + 2(NH_4)_2SO_4. \quad [3]$$

The initial reaction, represented by Eq. 1 and involving the mineral particles, water, ammonia, and dissolved oxygen, is heterogeneous while the subsequent oxidation of thiosulphate to thionate, sulphamate, and sulphate occurs homogeneously in the solution. Reaction rates are influenced by temperature, oxygen pressure, concentration of reactants in the solution, agitation of the pulp, and by the size of the mineral particles. Studies have shown that the rate of conversion of thiosulphate to thionates, sulphate, and sulphamate also is influenced by the presence in solution of cupric salts which act as oxidation catalysts.

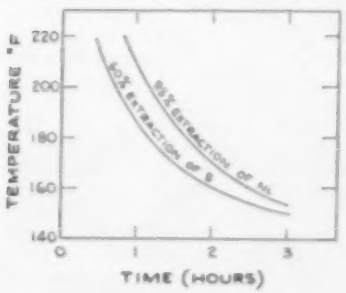

Fig. 3—Time required at different temperatures to effect the extraction of 95 pct of the Ni-60 pct S.

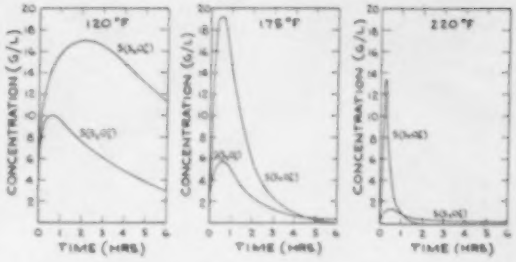

Fig. 4—Effect of temperature on the formation of $S_2O_3^{--}$ and $S_3O_6^{--}$.

Under the circumstances it is extremely difficult to determine with any certainty the rate-controlling factors except by inference from a series of batch tests carried out in such a way that one factor at a time is varied. As the leach is carried out commercially on a continuous basis, the steady state conditions present during operation are different from those found in a batch operation but the data obtained in the latter have been found to be entirely adequate for regulating the progress of the continuous leach.

Effect of Variables

The effect of variables on the rate and extent of the leaching reactions is briefly as follows:

Temperature: In a complex system it is not possible to predict the effect of temperature beyond the general statement that higher temperatures tend to increase reaction rates. This effect is complicated by the fact that higher temperatures tend to increase NH_3 vapor pressure and to promote hydrolysis. A series of experiments carried out with uniform conditions of agitation, O_2 pressure, pulp density, and initial solution composition but at different temperatures gave the results depicted in Fig. 3.

Although these curves indicate that there is a considerable advantage to be gained by using higher temperatures in the leach, this is offset by the fact that at the higher temperatures increased partial pressure of H_2O and NH_3 necessitates the use of higher total pressure to maintain adequate partial pressure of oxygen.

A further and more important factor is the requirement that the final leach solution produced in the first stage (where there is an abundance of fresh sulphide concentrate, a greater demand for oxygen, and a high evolution of heat) must contain a specific amount of thiosulphate and trithionate to provide the sulphide ions necessary for copper precipitation in the boiling operation which follows leaching. Reactions 1, 2, and 3 proceed simultaneously but each is affected differently by temperature variation. The effect of temperature on $S_2O_3^{--}$ formation in reaction 1, $S_2O_3^{--}$ formation in reaction 2, and $S_3O_6^{--}$ oxidation in reaction 3 is represented in Fig. 4, which shows the $S_2O_3^{--}$ and $S_3O_6^{--}$ concentration in a leach solution at successive periods of time in batch leaches carried out at 120°, 175°, and 220°F.

It is seen that by varying the temperature the peak of concentration of $S_2O_3^{--}$ or $S_3O_6^{--}$ may be varied, as may also the ratio of $S_2O_3^{--}$ to $S_3O_6^{--}$, and the period of time in which high concentrations of the two exist. The curves shown represent only one set of conditions in respect to oxygen pressure, agitation, liquid-solid ratio, and initial solution analysis: the progress of the reactions and hence the shape of the curves may be further varied by altering these conditions.

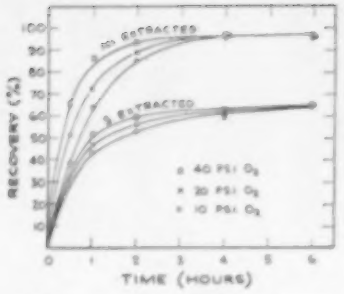

Fig. 5—Effect of O_2 pressure on extraction of nickel and sulphur.

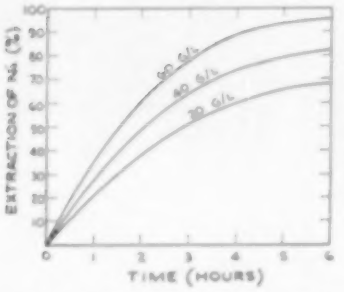

Fig. 6—Effect of unbound ammonia on the extraction of nickel (unbound NH_3 at 20, 40, and 60 g per liter.

Oxygen Pressure: During the early stages of a batch leach when fresh sulphides are abundant in the pulp, there is a high oxygen requirement for sulphide oxidation and for oxidation of thiosulphate and thionate to sulphate and sulphamate. Under these conditions, the concentration of oxygen in the solution becomes depleted and the leaching rate is determined by the dissolution of oxygen at the gas-liquid interface which in turn depends on the oxygen partial pressure.

As the leaching nears completion, the oxygen demand is less and oxygen pressure may be superseded as a rate-controlling factor by other factors such as outward diffusion of sulphide ions through the oxide layer surrounding the unreacted sulphide cores,[4] see Fig. 2.

In Fig. 5, which shows the amount of nickel and sulphur dissolved in the course of a series of leaches made at different oxygen pressures but with other conditions unchanged, it is seen that increased oxygen pressure accelerates the leaching action during the initial stages but has less effect on rate as the reactions proceed. Variation in oxygen pressure has no effect on the ultimate extraction of nickel or sulphur.

Increased oxygen pressure accelerates oxidation of thiosulphate and thionates during the initial period when they are abundant in the leach solution and thus tends to decrease the maximum concentration and life of the $S_2O_3^{--}$ and $S_4O_6^{--}$ ions in much

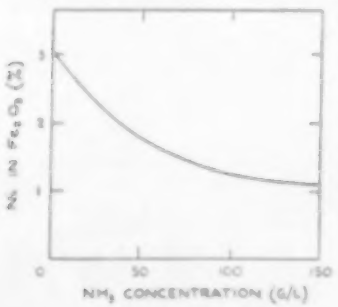

Fig. 7—Percentage of nickel in Fe_2O_3 as a function of NH_3 concentration.

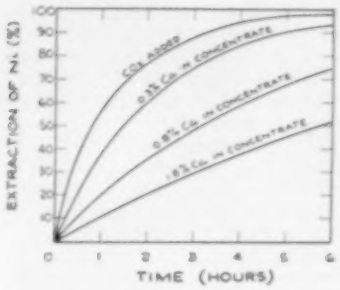

Fig. 8—Effect of soluble calcium on leaching rate of nickel.

the same way as these are affected by increased temperature, as shown in Fig. 4.

NH_3 Concentration: Determination of the effect of NH_3 concentration on the rate and extent of the leaching action is complicated by the fact that the ammonia entering the leach reacts in four ways: 1—some of the NH_3 is neutralized to NH_4^+, 2—some is converted to sulphamate $NH_2.SO_3^-$, 3—some joins the nickel, copper, and cobalt present to form ammines $[Ni(NH_3)x]^{++}$ in which x may have a value between 1 and 6, and finally 4—some NH_3 remains as unbound NH_3 in solution. The NH_3 in the metal ammines and the unbound NH_3 both react with acid and the sum of the two is termed "titrateable" ammonia. The proportion of each present can be determined[9] from a knowledge of the equilibrium constants for the formation of the various ammines.

Studies have shown that increased unbound NH_3 concentration within the range required for successful operation affects the leaching operation in two ways: 1—it increases the rate of leaching of nickel, copper, and cobalt and 2—it increases the maximum extraction of the metals. Fig. 6 illustrates these effects for the leaching of nickel; the curves for copper and cobalt are similar. The lower final extractions with low unbound NH_3 can be explained at least in part by the fact that high NH_3 content in the leach solution tends to reduce the nickel content of the hydrated iron oxide[10] as shown in Fig. 7. Varying the unbound ammonia does not affect the rate or extent of extraction of sulphur.

Sulphate Ions: If the concentration of anions such as sulphate ions is too low, the leaching rate and ultimate metal recoveries are also low. Normally, sufficient sulphur is dissolved from the sulphide concentrate to provide adequate concentration of sulphate and sulphamate ions in the leach solution. When leaching a sulphur-deficient material such as a matte or metal, it is necessary to provide additional anions in the leach solution, usually by the addition of ammonium sulphate.

Particle Size: The flotation concentrates used throughout the investigation were fine enough (about 85 pct −200 mesh) so that the minerals were largely unlocked and additional grinding had relatively little effect on leaching rate or recovery. It is obvious that coarser particles would leach more slowly due to the thicker oxide layer on the particle, increasing the difficulty of diffusion. The presence of particles of different sizes increases the difficulty of interpreting rate curves.

Calcium: The presence of soluble calcium in the concentrate, resulting from CaO additions in the flotation cells, has an adverse effect on the leaching rate. The extent of this effect has been determined by leaching a concentrate low in soluble calcium (0.3 pct), then adding different amounts of CaO, other conditions remaining unchanged. As shown

in Fig. 8, an addition of CaO corresponding to 0.5 pct of the concentrate, giving a total soluble calcium content of 0.8 pct in the concentrate, reduced the nickel leached in 6 hr from 95 to 75 pct while a 1.5 pct equivalent calcium addition reduced it to 50 pct.

It is presumed that the calcium combines with SO_4^{--} produced during leaching to form an insoluble $CaSO_4$ film on the surfaces of the leaching particles which, by obstructing the access of oxygen to the particles, retards the leaching action. The detrimental effect of calcium can be counteracted by adding a small amount of CO_2 to the leach solution to produce insoluble $CaCO_3$. The effect of CO_2 addition is indicated by the top curve in Fig. 8.

Agitation: Agitation has a pronounced effect on leaching rates due to the heterogeneous character of the reactions which involve dissolving oxygen at the gas-liquid interface, transporting the oxygen through the solution to the sulphide particles, and removing the concentrated leach solution from the liquid-solid interface. Any one of the three mentioned may be the rate-controlling factor at one time or another during the leach, but increased agitation which means increased power input will accelerate all three. Although this field has not been fully investigated, the data obtained indicate that the initial leaching rate of nickel is directly proportional to the power input. It should be mentioned that the practical limit of agitation is determined by the need to prevent disintegration of the comparatively soft hydrated iron oxide residue particles. Fine particles produced by overagitation are detrimental in subsequent thickening and filtering operations.

Boiling

The pregnant leach solution produced under conditions selected to give high recovery of metals in the two-stage continuous leaching unit is complex in character. It contains nickel, copper, and cobalt as ammines, unbound NH_3, $S_2O_3^{--}$, $S_4O_6^{--}$, SO_4^{--}, and $NH_4.SO_3^-$. The first step in treating this solution to prepare it for subsequent nickel precipitation has two objectives: 1—to remove and recover part of the titrateable NH_3 and 2—to separate the copper as sulphide. Both can be achieved by a single boiling operation, but, for purposes of convenience and efficiency, the copper removal is carried out in two stages.

In the first stage ammonia is boiled off in a series of pot stills, condensed, and recovered as 15 pct aqua which is recycled. In the second stage the solution low in unbound ammonia is heated to a temperature above 250°F to complete the precipitation of copper sulphide which commences as the ammonia concentration is lowered during the first boiling stage.

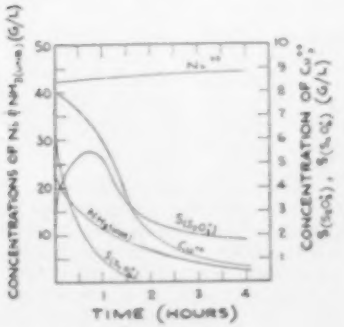

Fig. 9 — Progress of the boiling operation.

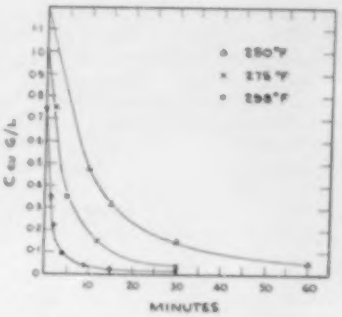

Fig. 10 — Influence of temperature on the precipitation of copper sulphide from ammine solution.

Reactions taking place as NH_3 decreases are as follows

$$S_2O_3^{--} + H_2O \rightarrow S_2O_4^{--} + SO_4^{--} + 2H^+ \quad [4]$$

$$S_2O_4^{--} + Cu^{++} + 2H_2O \rightarrow 2SO_4^{--} + CuS + 4H^+ \quad [5]$$

$$S_2O_3^{--} + Cu^{++} + H_2O \rightarrow SO_4^{--} + CuS + 2H^+ \quad [6]$$

$$8Cu^{++} + 2S_2O_3^{--} + 4H_2O \rightarrow 8Cu^+ + S_2O_6^{--} + SO_4^{--} + 8H^+ \quad [7]$$

$$2Cu^+ + S_2O_3^{--} + 2H_2O \rightarrow Cu_2S + 2SO_4^{--} + 4H^+ \quad [8]$$

$$Cu(NH_3)_4^{++} \rightarrow [Cu(NH_3)_{4-n}]^{++} + nNH_3 \quad [9]$$

$$Ni(NH_3)_6^{++} \rightarrow [Ni(NH_3)_{6-n}]^{++} + nNH_3 \quad [10]$$

The distillation of NH_3 from the leach liquor has been studied in some detail.[7] The problem can be treated as an ordinary NH_3 distillation operation providing consideration is given to the effect of metal ion concentration in the solution on the activity of the NH_3.

The progress of a boiling operation depicted in Fig. 9 shows that as NH_3 decreases the $S_2O_3^{--}$ decomposes rapidly and that the copper is precipitated by decomposition of both $S_2O_3^{--}$ and $S_4O_6^{--}$. After three hours, the rate of precipitation of copper becomes uneconomically slow.

In the second stage, the boiled solution containing copper sulphide is transferred to an autoclave and the temperature raised to 250°F or over to accelerate the final precipitation of CuS by $S_4O_6^{--}$, according to reaction 6. The effect of increasing temperature is shown in Fig. 10. In actual operation, the boiling and copper sulphide precipitation are carried out in continuous units, the copper being reduced to 0.03 to 0.1 g per liter.

Stripping

As it is necessary that the copper concentration in the boiled solution be less than 0.005 g per liter, further purification is required. This is readily achieved by adding H_2S in stoichiometric amount at solution temperatures of about 200°F. The final purified solution contains about 0.001 g per liter Cu. If H_2S is not available, a similar purification can be effected by heating the solution to about 300°F in the presence of fresh nickel concentrate or pyrrhotite. By a replacement mechanism, the copper is precipitated as sulphide.

Application of Principles in Pilot Plant Control

In the pilot plant leaching operation, the countercurrent leach, boiling, copper removal, and copper stripping operations are all carried out in continuous units. In such an operation the steady state conditions existing at a given time and in a given unit are necessarily different from those occurring at any time in a batch operation. The interpretation

of data obtained in batch tests in terms of continuous operation must depend therefore on empirical relations which can be established only on the basis of adequate experimental results and correlation of batch and continuous data. Nevertheless, the principles and trends observed in batch tests do serve as a guide in developing design and in controlling the chemistry of the continuous units.

It is evident from the basic studies that the critical factors in the leaching circuit are: temperature, ammonia concentration, oxygen pressure, and agitation.

Since the oxidation of sulphides in solution generates large amounts of heat, the regulation of temperature can be simply effected by altering the amount of water in the cooling coils and jackets which surround the autoclaves. In the pilot plant temperature is controlled automatically by a thermoregulator on the cooling water discharge. The optimum operating range is between 160° and 175°F. In this range the leaching reaction proceeds rapidly and the concentration of thiosulphate and polythionate in the pregnant solution is sufficient to precipitate the copper in the subsequent boiling operation. The concentration of thiosulphate and thionate can be increased by reducing the leaching temperature. It is possible to regulate $S_2O_3^=$ content within 1 g per liter by changing the temperature 5°F without changing the leaching rate by a measureable amount.

To ensure maximum extraction of metals, the NH_3 content of the leach solution is maintained at the highest value compatible with efficient operation. Usually the unbound NH_3 is carried at 50 to 60 g per liter. A deficiency of NH_3 in the second stage of leaching lowers recoveries and very high NH_3 imposes a heavy load on the absorption towers used for stripping NH_3 from the effluent gases from the autoclaves. The NH_3 content is regulated by periodic titration of the leach solutions and maintained by automatic NH_3 feeding devices linked to the ore input to the leaching system. The unbound NH_3 content of solution can be readily controlled within ±5 g per liter.

Oxygen pressure has a less important effect than temperature or NH_3 concentration and is not usually varied but is determined by the operating pressure of the autoclaves, the temperature, and the partial pressure of NH_3. The autoclaves operate at about 100 psig and O_2 in the effluent gases is about 8 pct, giving an oxygen efficiency of 60 to 70 pct. Higher efficiencies can be obtained but only at the expense of lowered leaching rates, due to oxygen deficiency in leach solutions when the partial pressure of oxygen is reduced to a low level. Higher leaching temperatures and high NH_3 content of the leach solution increase the partial pressure of NH_3 and, as the total pressure remains unchanged at 100 psig, effectively reduce the oxygen partial pressure, thus tending to reduce the leaching rate and to counteract the advantage to be gained by higher temperature and NH_3 concentration.

The agitation must be sufficient to maintain a uniform pulp, to provide the maximum gas-liquid interface to promote oxygen dissolution, and to produce a "shearing" action at the surface of particles. Increased agitation is obtained only at the expense of additional power. The amount of agitation to be used therefore is determined largely by economic considerations and by the requirement already noted that the soft leached particles must not be abraded. The quality and degree of agitation are regulated by using different types of impellers driven by variable speed motors.

In the boiling and copper removal stages, the batch data are translated to continuous operation without difficulty.

The continuous boiling unit is operated to produce 15 pct aqua in the ammonia condenser, the rate of flow being adjusted to the heat input into the evaporators. Water and steam are added to maintain a uniform liquid volume in order to prevent precipitation of nickel salts from a concentrated solution.

The continuous copper precipitation unit is designed in such a way that the retention time is sufficient to permit reducing the copper content of the solution to about 0.03 g per liter at 250°F. As this is a homogeneous reaction, the important factor is temperature and the time required can be regulated by adjusting the temperature. The operation is readily controlled.

The stripping reaction is controlled by feeding continuously a measured (stoichiometric) amount of H_2S to the reaction vessel. Temperature and agitation can be varied to regulate the retention time necessary for complete removal of copper.

Summary

In the ammonia pressure leaching process for extracting nickel, cobalt, copper, and sulphur from sulphide minerals, the reactions in the leaching stage which are heterogeneous in character are such that oxygen dissolves in an ammoniacal leach liquor and there reacts with the solid sulphides to give oxidized products including nickel, cobalt, and copper ammines, sulphate, thiosulphate, polythionate and sulphamate ions, and hydrated ferric oxide.

The rate of leaching is controlled by temperature, NH_3 concentration in the leach liquor, oxygen pressure, and amount of agitation. Of these, temperature and NH_3 concentration are the most important although adequate oxygen and agitation must be provided. The leaching operation is regulated to produce a pregnant liquor having a content of thiosulphate and polythionate sufficient to react with the copper present in the subsequent boiling stage and to produce an iron oxide residue low in adsorbed nickel.

The pregnant liquor is boiled to produce 15 pct aqua and to lower the unbound NH_3 to the point where thiosulphate and polythionates decompose by reaction with copper ions to produce copper sulphide. In a second copper-removal stage, the temperature of the boiled solution is raised to over 250°F to accelerate the decomposition of thiosulphate and to precipitate the copper to 0.03 g per liter. The copper is finally reduced to 0.001 g per liter by addition of a measured stoichiometric amount of H_2S.

The final copper-free solution, containing about 45 g per liter Ni, 0.8 g per liter Co, 0.001 g per liter Cu, in addition to sulphur as sulphate and sulphamate in an amount of 80 to 90 g per liter, is in suitable condition for the subsequent operations associated with precipitation of nickel.

Acknowledgments

The studies which have resulted in the development of the detailed knowledge of the chemistry of the leaching process have been carried out by the staff of the Sherritt Gordon Metallurgical Research Div. Those most closely associated with this have been Mrs. A. M. Armstrong, R. L. Benoit, W. Hermann,

V. Kunda, and W. C. Lin. To each of them the authors are indebted.

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Acid Pressure Leaching of Uranium Ores

by F. A. Forward and J. Halpern

A new process is described for extracting uranium from ores containing sulphidic minerals, which comprises treating an aqueous pulp of the ore with air or oxygen at elevated temperatures and pressures. The acid required to dissolve the uranium is generated during the leach through oxidation of the sulphides. The chemistry of the process is discussed and laboratory results are presented to illustrate the operation of the method and the variables which control it. With most ores, leaching at a temperature of 130°C and an oxygen partial pressure of 10 psi provides uranium extractions of 90 to 95 pct in 4 to 6 hr. The acidity and level of dissolved impurities in the leach liquor can be kept fairly low. The method is characterized by a number of advantageous features including low reagent cost, short retention times, and high recoveries.

RECENTLY there have been developed several processes for extracting metal values from ores by pressure leaching techniques;[1-5] an example is the carbonate leaching process for uranium ores which has been studied in this laboratory.[1] Leaching is carried out under oxygen pressure to ensure oxidation of the uranium to hexavalent compounds which are soluble in carbonate solutions.

During the course of investigations relating to this process, it was observed that sulphide minerals, such as pyrite, usually were oxidized under the conditions of the leach treatment resulting in the formation of iron hydroxides and sodium sulphate, i.e.

$$2\ FeS_2 + 7\tfrac{1}{2}\ O_2 + 8\ Na_2CO_3 + 7\ H_2O \rightarrow 2\ Fe(OH)_3 + 4\ Na_2SO_4 + 8\ NaHCO_3 \quad [1]$$

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A similar reaction involving the oxidation of pyrite in sodium hydroxide solutions has recently been studied by Stenhouse and Armstrong.[4]

Reaction 1 may be considered as taking place in two steps represented by the following equations

$$2\,FeS_2 + 7\tfrac{1}{2}\,O_2 + 7\,H_2O \rightarrow 2Fe(OH)_3 + 4\,H_2SO_4 \quad [2]$$

$$4\,H_2SO_4 + 8\,Na_2CO_3 \rightarrow 4\,Na_2SO_4 + 8\,NaHCO_3 \quad [3]$$

The reagent consumption resulting from these reactions often renders carbonate leaching uneconomical for the treatment of high sulphide uranium ores. It has also been found that such ores are sometimes difficult to treat by conventional acid leaching because of excessive reagent consumption, poor recoveries, or large amounts of impurities dissolved.

The process described in this paper is designed to overcome these difficulties and to provide a simple and economical method for extracting uranium from sulphidic ores. Based on the observations and considerations outlined previously, it takes advantage of the presence of sulphur or sulphidic minerals in the ore, using them to generate the acid required to dissolve the uranium, thus making it possible to leach the ore with water to which no acid or other leaching reagents have been added.

The method comprises treating an aqueous pulp of the ore with air or oxygen at elevated temperatures and pressures. The sulphides in the ore are oxidized in accordance with Eq. 2 or through similar reactions, and the solution is thus rendered sufficiently acidic to attack and dissolve the uranium minerals. The combination of elevated temperatures and oxygen pressures ensures that leaching is rapid and complete. By suitably controlling the conditions of the leach, it is possible to maintain the acid and dissolved impurities at conveniently low levels.

This process has been examined on a laboratory scale and found to operate efficiently for a variety of uranium ores ranging in grade from 0.08 to 0.60 pct U_3O_8 and in sulphur content from 1 to 13 pct; the ores varied widely in origin and mineral constitution. Some typical results, illustrating the application of the method to recovering uranium from one of these ores, are presented in this paper.

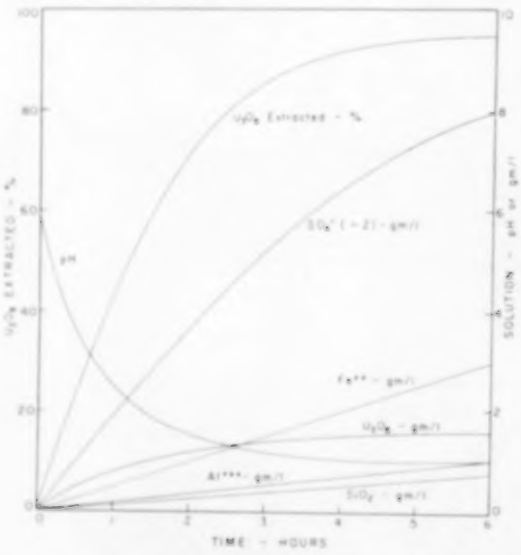

Fig. 1—Course of a typical leaching experiment. Grind, 65 pct −200 mesh; pulp density, 50 pct solids; temperature, 130°C; and O_2 pressure, 10 psi.

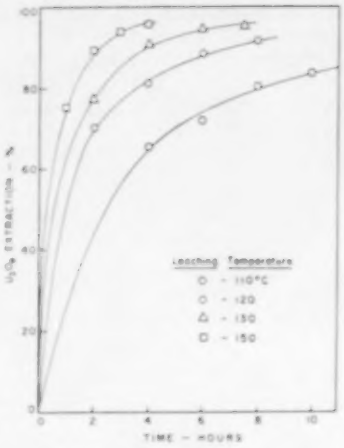

Fig. 2—Leaching-rate curves at different temperatures. O_2 pressure, 10 psi.

Experimental

Materials: The ore used in these tests had the following composition: U_3O_8, 0.17 pct; Fe, 3.8 pct; S, 4.4 pct; Al_2O_3, 1.3 pct; CaO, 0.1 pct; MgO, a trace; and SiO_2, 89.0 pct. The uranium was present chiefly as finely disseminated pitchblende or uraninite. Pyrite, together with a small amount of pyrrhotite, accounted for most of the iron and sulphur.

The leaching tests were made using distilled water and compressed oxygen of commercial grade. All chemical reagents were chemically pure grade.

Procedures: The leaching tests were conducted in an autoclave, measuring 7 in. ID by 11 in. in height, and constructed entirely of No. 316 stainless steel. The autoclave was heated externally with a gas burner, the temperature being regulated by a Wheelco thermocouple controller. A thermocouple well, cooling coil, sampling tube, and externally driven impeller shaft were sealed through the bolted lid. The impeller had three pitched blades of 1.5 in. radius and was rotated at 550 rpm.

The charge generally consisted of 2000 g of water and 2000 g of ore, rod milled to a desired screen size (usually 65 pct −200 mesh). It was heated in the autoclave to a given temperature and maintained, with continuous stirring, under a desired partial pressure of oxygen. The ore and solution were sampled periodically and analyzed. Uranium extractions were calculated in all cases from tailings analyses.

Uranium determinations were made fluorimetrically[5] using a Massachusetts Institute of Technology Model III Fluorimeter. pH measurements were made with a Beckman Model H2 pH Meter. Other determinations were by standard analytical methods.

Results and Discussion

Course of a Typical Leach: Fig. 1 depicts the course of a typical leaching experiment made under the following conditions: grind, 65 pct −200 mesh; pulp density, 50 pct solids; temperature, 130°C; O_2 pressure, 10 psi; and total pressure, 35 psig.

These conditions were found to result in rapid oxidation of the sulphides so that the pH of the

solution was lowered to a value of 1.0, and 16 g per liter of SO_4^{--} was dissolved in about 6 hr. During this period, about 95 pct of the uranium in the ore was leached. The final composition of the leach solution was: U_3O_8, 1.6 g per liter; Fe^{++}, 3.0 g per liter; Al^{+++}, 1.0 g per liter; SiO_2, 0.8 g per liter; and SO_4^{--}, 16 g per liter.

The leaching behavior of the other ores which were tested was similar and, in each case, comparable extractions were obtained under the same conditions.

Chemistry of the Leach Process: In addition to the reaction represented by Eq. 2, reactions of the following type probably enter into the oxidation of the pyrite during the leach

$$FeS_2 + 3\tfrac{1}{2}\ O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4 \quad [4]$$

$$2\ FeS_2 + 7\tfrac{1}{2}\ O_2 + H_2O \rightarrow Fe_2(SO_4)_3 + H_2SO_4 \quad [5]$$

$$Fe_2(SO_4)_3 + (3 + x)\ H_2O \rightarrow Fe_2O_3 \cdot xH_2O + 3\ H_2SO_4 \quad [6]$$

$$Fe_2(SO_4)_3 + (2 + 2x)H_2O \rightarrow 2\ Fe(OH)SO_4 \cdot xH_2O + H_2SO_4 \quad [7]$$

and so forth. All these reactions yield sulphuric acid; some also result in the formation and dissolution of iron salts. Nearly all the iron in solution was in the form of ferrous sulphate. Apparently any ferric salts which are formed are hydrolyzed in accordance with Eqs. 6 and 7 and precipitated as hydrated ferric oxides or basic ferric sulphates. This is to be expected in view of relatively high temperatures and low acidity of the leach solutions.

Elemental sulphur and other sulphide minerals such as pyrrhotite can be oxidized in a similar manner and also yield sulphuric acid under the conditions of this leach treatment, i.e.

$$S + 1\tfrac{1}{2}\ O_2 + H_2O \rightarrow H_2SO_4 \quad [8]$$

$$2\ FeS + 4\tfrac{1}{2}\ O_2 + (x + 2)H_2O \rightarrow Fe_2O_3 \cdot xH_2O + 2\ H_2SO_4 \quad [9]$$

Most uranium minerals are readily attacked and dissolved by the acid solutions thus generated. In the case of pitchblende or uraninite, the leaching reaction is

$$U_3O_8 + \tfrac{1}{2}\ O_2 + 3\ H_2SO_4 \rightarrow 3\ UO_2SO_4 + 3\ H_2O. \quad [10]$$

Other uranium minerals react in a similar manner and also dissolve as uranyl sulphate. These reactions are favored by the high temperatures and oxygen pressures which are used, permitting shorter retention times to be employed and higher recoveries to be obtained than is often possible with conventional acid leaching.

The dissolution of small amounts of aluminum, magnesium, and silica which is sometimes observed can be attributed to the reactions

$$Al_2O_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2O \quad [11]$$

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O \quad [12]$$

$$SiO_2 + H_2O \rightarrow H_2SiO_3 \quad [13]$$

Other metals in the ore, which form soluble sulphates and which are not readily hydrolyzed, also might be expected to dissolve.

Leaching Variables: 1—**Grind**—While the leaching rate generally increased with the fineness of grind, a grind of 50 to 60 pct −200 mesh was found to be satisfactory with most ores and to yield optimum recoveries of 90 to 95 pct U_3O_8 with fairly short retention times.

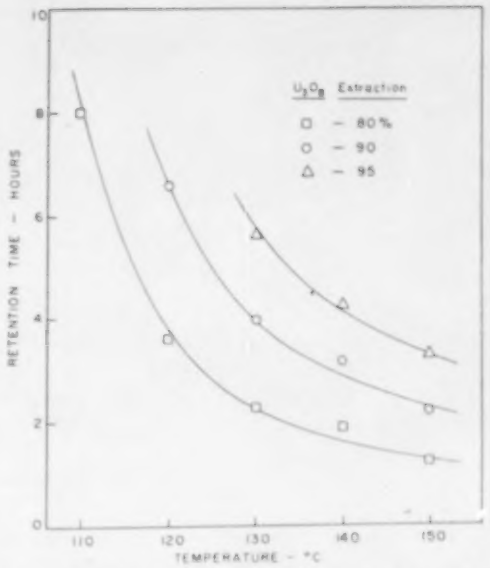

Fig. 3—Relation between temperature and retention time. O_2 pressure, 10 psi.

2—**Pulp Density**—No changes in the leaching rate, or in the ratio of the concentrations of dissolved impurities to that of uranium, were observed when the pulp density was varied from 20 to 65 pct solids. A pulp density of about 65 pct solids appears to be practical and advantageous.

3—**Temperature**—Temperature was found to be the most critical variable affecting leaching rates and recoveries. This is illustrated in Figs. 2 and 3, which show that the leaching rate doubles and the retention time required to achieve a given extraction is correspondingly reduced with every rise in temperature of 10° to 15°C. Thus it would appear desirable to operate at temperatures of 130° to 140°C, where 4 to 6 hr are generally required to achieve recoveries of 95 pct U_3O_8. Below 120°C, oxidation of the sulphides and leaching of uranium are usually impracticably slow.

4—**Oxygen Pressure**—As would be expected, no acid was generated and no uranium dissolved in the absence of oxygen. On introducing oxygen, the leaching rate was found to increase with the oxygen partial pressure up to partial pressures of about 10 to 15 psi; further increases in the oxygen partial pressure had little effect. This is shown in Fig. 4. The optimum partial pressure of oxygen thus would appear to be about 10 psi, corresponding to 50 psi of compressed air. At 130°C the vapor pressure of the solution is about 25 psig. Total operating pressures would thus be about 35 psig if oxygen is used or 75 psig if air is used.

Recycling: It was found that the leach solutions could be recycled, if desired, to increase the concentration of U_3O_8 up to 4 to 5 g per liter or higher. Leaching was usually considerably more rapid in the second cycle than in the first, presumably because of the acid already present in the solution. At the same time, it was found that the amount of

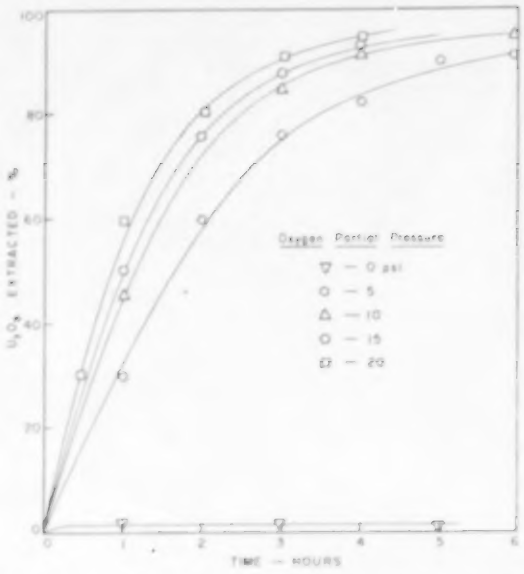

Fig. 4—Leaching-rate curves at various oxygen pressures. Temperature, 130°C.

acid generated and impurities dissolved in the second cycle were lower than in the first. Consequently, a better ratio of uranium to impurities was obtained, facilitating subsequent treatment of the solution.

Corrosion: No practical difficulties were encountered in carrying out these leaching experiments on a laboratory scale using an autoclave constructed of No. 316 stainless steel. Providing the temperature was maintained below 140°C and the oxygen partial pressure below 15 psi, there was no evidence of any serious corrosion. Some pitting corrosion was observed when higher partial pressures of oxygen were used, but this would not appear to be a serious consideration, since it has been shown that satisfactory leaching can be achieved at oxygen pressures of 10 psi or less.

Precipitation: Any of the known methods of precipitating uranium from acid solutions can be applied to recover the uranium values from the leach liquors obtained by this treatment. A particularly convenient method consists of raising the pH of the solution to a value of 6 or higher by addition of ammonia. This precipitates all the uranium as an ammonium uranate salt, together with hydroxides of iron and aluminum. The precipitate obtained by this method usually contains 10 to 20 pct U_3O_8.

Since the leaching method permits the concentrations of free acid and/or iron salts in the solution to be maintained at low levels, the amount of ammonia which is required for this precipitation is fairly low, usually about 10 per lb per ton. If desired, the crude precipitate which is obtained may be further upgraded by igniting or by leaching with a carbonate solution which dissolves the uranium, separating it from the iron and aluminum hydroxides. A high grade uranium product, assaying 70 to 80 pct U_3O_8 can be recovered readily from the carbonate solution by addition of caustic. The barren liquor from the ammonic precipitation contains ammonium sulphate and can be discarded, recycled, evaporated to recover ammonium sulphate, or treated with lime to recover the ammonia.

Conclusions

A new process has been described for extracting uranium from ores containing sulphidic minerals. This process, which has been developed and tested on a laboratory scale, comprises treating an aqueous pulp of the ore with air or oxygen at elevated temperatures and pressures. The acid necessary to dissolve the uranium is generated during the leach by oxidation of the sulphides. This makes it possible to leach the ore with water to which no acid or other leaching reagents have been added. The sulphur or sulphidic compounds used to generate the acid may be present originally in the ore, or they can be added. In this way, the process can be applied to most uranium ores.

Laboratory results have been presented which illustrate the application of the process and the chemical reactions and variables which control it. With most ores the following leaching conditions appear to be optimum: grind, 50 to 65 pct −200 mesh; pulp density, 65 pct solids; temperature, 130°C; and O_2 partial pressure, 10 psi. Under these conditions, uranium extractions of 90 to 95 pct were obtained with all the ores examined, including one ore which gave recoveries of only 50 to 60 pct by conventional acid or carbonate leaching. Retention times of 4 to 6 hr were usually adequate.

Among the advantages which appear to be associated with this porcess, are the following:

1—No reagents other than compressed air or oxygen are required in the leach.

2—The retention times are usually much shorter than with conventional methods. The resulting reduction in the size of leaching vessels serves to compensate for the use of higher temperatures and pressures.

3—Higher uranium extractions are often obtained than by conventional leaching methods.

4—The acidity and level of dissolved impurities in the leach liquors can be kept fairly low. This facilitates recovery of the final uranium product.

It is suggested that the method can be applied with particular advantage to recovering uranium 1—from ores whose sulphide content is so high that excessive reagent consumption is entailed in using other methods, and 2—from ores containing refractory uranium minerals where recoveries by other methods are often unsatisfactory.

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Preparation and Arc Melting of High Purity Iron

by G. W. P. Rengstorff and H. B. Goodwin

A method is described for purifying iron in batches of 150 lb or more. Oxygen, carbon, nitrogen, and sulphur are removed from flakes of electrolytic iron by treatment in wet and then dry hydrogen. A special consumable-electrode arc furnace is used to remove hydrogen and to melt the flakes into ingots.

ALTHOUGH iron and steel have been made and used for hundreds of years, there are still wide gaps in the knowledge of these metals. One reason for this is that the true properties of the base metal, iron, are not well known, simply because really pure iron has never been readily available for research purposes.

Commercial iron, and even the "pure" irons which are readily available, are really complex alloys of iron with oxygen, nitrogen, hydrogen, carbon, sulphur, silicon, and other elements. With such materials, it has not been possible to prepare steels and other iron-base alloys in which all elements are present in exactly controlled amounts. It is an almost impossible task to determine the separate effects of each element or the intereffects of several elements unless alloys can be prepared containing only the desired elements.

The ability to make controlled alloys of low impurity content is of far more than academic interest. It will assist in the study of such practical problems as the brittle failure of ship hulls or high pressure gas pipelines, determination of the factors which affect the deep-drawing properties of steels, the improvement of magnetic and electrical properties, the phenomenon of aging, and many others.

In 1949, the American Iron and Steel Institute asked Battelle Memorial Institute to prepare high purity iron on a larger scale than had been attempted up to that time. The work was directed toward the preparation of iron as low as possible in carbon, oxygen, nitrogen, hydrogen, and sulphur because these are the contaminating elements of major interest in many research investigations on iron-base alloys. The initial goal was to prepare iron with not more than a few thousandths of one percent of each of these impurities. The purpose was to set up a "bank" of high purity iron on which researchers could draw when a supply was needed and which could be replenished from time to time as the stock became depleted.

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Of several possible purification methods, heating in hydrogen was selected as the most promising for the removal of both carbon and oxygen from solid iron. Metallic impurities are not removed by hydrogen. Electrolytic iron was chosen as a starting material because it is the most readily available form of iron low in metallic impurities.

Decarburization and desulphurization were obtained by annealing in wet hydrogen at relatively low temperatures. The optimum temperature, as found by previous investigators,[1] is about 1400°F. This treatment also removes nitrogen.

Deoxidation is favored by dry hydrogen and higher temperature. There is evidence from previous work that an anneal at 2200°F in dry hydrogen will deoxidize the iron, reduce the nitrogen content, and reduce the sulphur content.

These facts suggested the use of a two-stage process: treatment in wet hydrogen followed by treatment in dry hydrogen.

To carry out the purification process in a reasonable time, it was necessary that the iron be in thin pieces. Flakes of electrolytic iron were used. Because most research requires that the iron be in massive form, it was necessary to melt the purified iron to consolidate it into large pieces. For this work, it was decided to prepare ingots weighing at least 15 lb by using a cold hearth arc-melting process in which the iron was melted in an inert atmosphere of argon or helium. This method of melting was selected because the water-cooled copper crucible is not wet by the iron and does not contaminate it as a refractory crucible would. Because the crucible is also the ingot mold, contamination from mold materials was also eliminated. Contamination from electrodes was avoided by making them from purified electrolytic iron. The melting procedure finally developed was an adaptation of the Kellogg electric ingot process.[2]

Two batches of purified iron weighing about 100 lb each in ingot form were prepared with analyses as shown in Table I.

The remainder of this paper describes the procedures in more detail. In general, the process con-

sists of four major steps as follows: 1—preparation of electrodes from flakes of electrolytic iron, 2—treatment of the electrodes with wet hydrogen, 3—treatment of the electrodes with dry hydrogen, and 4—arc melting of the purified electrodes into ingots.

Preparation of Electrodes

The first step was to make electrolytic iron sheet 0.03 in. thick. This was done by induction melting electrolytic iron flakes in a MgO crucible under a blanket of argon and casting an ingot. The ingot was forged and rolled into sheet which was cut into pieces which would form tubes 2 in. in diameter and 72 in. long, as shown in Fig. 1.

The tube was closed by tack welding, one end was crimped closed, and the tube was filled with flakes of electrolytic iron with a little steel wool in the open end to hold the flakes in position. An electrode, complete except for the steel wool, is shown in Fig. 2.

Flakes of electrolytic iron received from the manufacturer were about ¾ in. on their longest dimension, too large to pack tightly into the electrodes. The flakes were easily broken to a more convenient size (about ¼ in. or less) by putting them through a hammer mill with the lower screen removed.

Assembly for Purification in Hydrogen

Seven electrodes were packed into an assembly which consisted of an electrolytic-iron tube inside a mild steel jacket, as shown in Fig. 3.

The double-wall construction was used to prevent diffusion of gases into the purification zone by maintaining a flow of argon in the space between the tubes; gases which diffused through the outer tube were swept away. Not shown in Fig. 3 is a type 321 stainless steel separator between the inner tube and the jacket. The stainless steel slowed the passage of carbon from the jacket (0.15 to 0.25 pct C) to the inner tube (0.005 pct C).

It was necessary to use low carbon iron (electrolytic iron) for the inner tube. Unless this was done, carbon from the inner tube was transferred to the electrodes. This was strikingly shown in one test in which the inner tube was 1020 steel. In this test, the ends of the electrodes near the hydrogen inlet contained less than 0.001 pct C, but the rest of the electrodes contained about 0.023 pct C.

Fig. 1—Tube for electrode before welding.

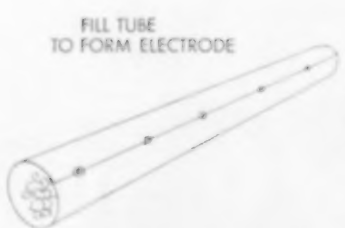

Fig. 2—Electrode after welding, crimping, and packing.

Table I. Carbon, Oxygen, Nitrogen, and Hydrogen Analyses of Ingots

	Analysis, Pct			
	Oxygen*	Nitrogen*	Hydrogen*	Carbon†
Ingots Purified in Lot 1‡				
A9854, c††	0.0022	<0.0002	0.00002	0.003
A9855, b	0.0024	0.0001	0.00001	0.005
A9857, c	0.0061**	0.00009	0.000016	0.004
	0.0060	0.00007	0.000053	
A9858, b	0.0023	0.0004	0.00002	0.006
B252, c	0.0049**	<0.00007	0.000026	0.004
B253, c	0.0028	<0.00009	0.000019	0.004
Ingots Purified in Lot 2				
A9859, b††	0.0010	<0.0002	0.00002	0.005
B254, c	0.0010	<0.00009	0.000025	0.004
B255, c	0.0023	<0.00009	0.000025	0.004
B256, c	0.0016	<0.00008	0.000019	0.007
B257, c	0.0011	<0.00008	0.000027	0.005
B258, c	0.0012	<0.00008	0.000016	0.003
B259, b	0.0016	0.0003	0.0001	0.005

* Oxygen, nitrogen, and hydrogen analyses were made by the vacuum-fusion method.

† Carbon analyses were made by a combustion method. Products of combustion were measured by a conductometric method.

‡ One ingot in lot 1 was spoiled, so it was not analyzed.

** These ingots were apparently contaminated with water vapor while being arc melted.

†† Analyses were made on these ingots as cast. All other analyses were made on ingots which had been forged and annealed.

Estimated accuracy of analyses based on sensitivity of the apparatus: oxygen, ingots marked *a*, ±0.00010 (1 ppm); ingots marked *b*, ±0.00010 (1 ppm); and ingots marked *c*, ±0.00005 (0.5 ppm). Nitrogen, ingots marked *a*, ±0.00020 (2 ppm); ingots marked *b*, ±0.00010 (1 ppm); and ingots marked *c*, ±0.00008 (0.8 ppm). Hydrogen, ingots marked *a*, ±0.000020 (0.2 ppm); ingots marked *b*, ±0.000010 (0.1 ppm); and ingots marked *c*, ±0.000006 (0.06 ppm).

Variations of estimated accuracy are due to the vacuum-fusion analyses being made at different times with several pieces of equipment during a period of a year.

Electrolytic-iron plate for the inner annealing tube was rolled from a 500 lb ingot to a thickness of ¼ in.* Considerable trouble was encountered with cracking of the electrolytic plate while forming it into a tube.† This problem was partially solved by normalizing the plate at 1500°F before forming. The inner tube was fabricated as two sections, each 7 1/3 in. ID and 45 in. long. The two sections were welded together into a 90 in. tube, a flange was welded to one end, and a bottom plate to the other. Heliarc welding was used with electrolytic iron as a filler. The tube was made as gas tight as possible.

* Rolling was done by Universal-Cyclops Steel Co., Bridgeville, Pa. Forming was done by the Pearson Manufacturing Co., Pittsburgh.

† That an iron which is high in oxygen and low in carbon and manganese should be brittle is in good agreement with the findings of Rees and Hopkins.[8]

The outer jacket, a 10 in. grade *A* seamless steel pipe with ½ in. walls, protected the inner tube from furnace gases. Although it was sprayed with aluminum to reduce oxidation, it oxidized so severely that it had to be replaced after each run.

The entire annealing tube assembly was arranged so that it could be evacuated before filling with hydrogen. Also, it could be flooded with argon as a safety measure.

Treatment in Wet Hydrogen

The assembled annealing tubes containing electrodes were placed in a gas-fired semimuffle furnace as shown in Fig. 4, connected to a system for continuously supplying hydrogen, and the furnace heated to 1400°F.

In the first run, tank hydrogen was introduced directly into the annealing assembly. There was enough oxygen in the iron to produce wet hydrogen for 6 hr, the length of the wet hydrogen treatment in the first run. In the second run, the 1400°F an-

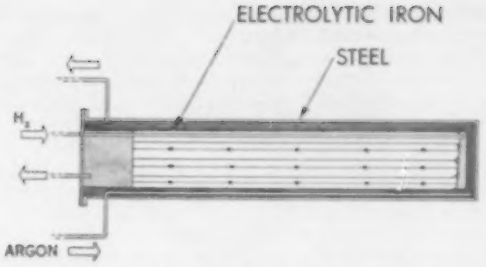

Fig. 3—Schematic diagram of the purification tube assembly.

neal in wet hydrogen was continued for 32 hr. To do this, the hydrogen was saturated by bubbling it through water at 160°F. Arrangements were made to prevent condensation of the water in the lines to the annealing assembly. There is not yet any clear-cut evidence that the 32 hr treatment was any more effective than the 6 hr treatment. A still longer anneal in wet hydrogen, however, might be beneficial.

Treatment in Dry Hydrogen

After the wet hydrogen treatment, the furnace temperature was raised rapidly from 1400° to 2100°F and then slowly from 2100° to 2300°F. The temperature in the tube was usually about 50°F lower than that of the furnace. Dry purified hydrogen was flowed through the annealing assembly until the dew point of the exit gas dropped to about −30°F for the first run and −38°F for the second run. Times for the dry hydrogen treatment were 51 and 65 hr, respectively.

Although several complicated systems were used for the purification of hydrogen in early experiments, it was found that the most satisfactory results were obtained by simply passing the gas through hot titanium turnings or sponge. Systems which did not include hot titanium as one step were all unsatisfactory; they did not remove hydrocarbons from the tank hydrogen. These hydrocarbons caused contamination of the iron by carbon.

For the first run, titanium sponge was heated continuously at 1600°F, the sponge packed, and the hydrogen channelled through it. For the second run, thin layers of sponge were alternated with thin layers of machined titanium turnings. The layered titanium mixture was heated to 1500°F, soon raised to 1550°F, held there for most of the run, and then gradually raised to 1700°F shortly before the end. This procedure gave very satisfactory results.

Although details are not shown in Fig. 5, the hydrogen system included valving so that either wet hydrogen or dry hydrogen could be furnished to the annealing tube. The system also permitted argon to be flowed into the annealing tube when desired and included a vacuum pump to evacuate the tube. Suitable traps were provided along with flow meters, dew-point meter, and a cone to burn the exit hydrogen. All tubing leading to the annealing furnace was copper and connected with flared fittings. The system was checked periodically to be sure that it remained gas tight.

At the end of the first run, a hole developed in the jacket of the annealing tube so the system was flooded with argon and cooled. The second batch was cooled in dry hydrogen to 1100°F, then in argon to room temperature.

Arc Melting the Purified Electrodes Into Ingots

The hollow electrodes filled with loose flakes introduced a problem not encountered with solid consumable electrodes. Because electrical contact between the flakes was poor, practically all of the current was conducted by the thin iron tube which became heated by resistance and tended to melt high above the arc. To avoid this, the current had to be introduced into the electrode as close to the arc as possible. Because the electrode had to move downward as it melted, a movable contact was required. Sliding or rolling contacts, however, have a tendency to arc at the high currents required, especially on surfaces as rough as these electrodes. Arcing between the electrode and the contact welds the electrode to the contact or contaminates the high purity electrode with metal from the contact.

A new contact in which the electrode was gripped alternately by two sets of jaws was the solution to the problem. One set of jaws is movable and connected to the electrical source by a short link of flexible cable. The electrode feeds down with the movable jaws firmly clamped to it. When the end of the travel of the jaws is reached, the electrode is gripped by a set of fixed jaws while the movable jaws loosen and move upward to get a new grip on the electrode. Each set of jaws grips before the other lets go so there is no break in the flow of current.

The electrode clamp is shown in Fig. 6. An arrangement of a weight and lever exerts pressure on a wheel which forces the electrode against fixed and movable shoes. The electrode is held tightly between the moving shoe and pressure wheel while the shoe is driving the electrode downward. This shoe is actuated by a cam driven from outside the furnace. When the jaw has reached its maximum downward stroke, the cam moves the jaw back out

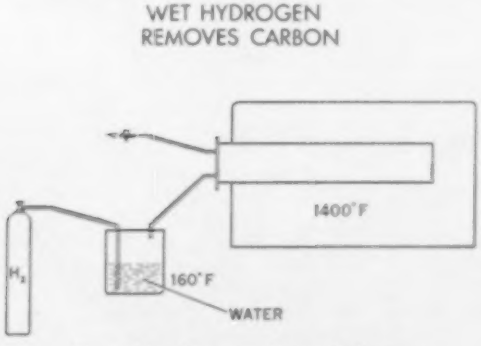

Fig. 4—Annealing setup for wet hydrogen.

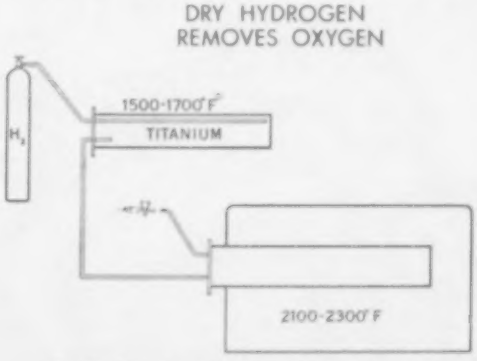

Fig. 5—Setup for annealing with dry hydrogen.

Table II compares the nonmetallic impurity con-

of the way for its upward stroke. Meanwhile, the electrode is held tightly between the fixed shoe and the pressure wheel. At the top of the stroke, the moving jaw again takes over to give the electrode another short downward movement.

Fig. 7 shows the arrangement of the furnace for melting the electrodes. The water-cooled base plate for the first ingots was copper brazed to steel. After the braze cracked because of a difference in thermal expansion of the two metals, the base plate was made entirely of steel. The sides of the crucible were water-cooled copper.

The furnace was evacuated and flushed with argon twice before starting each melt. An atmosphere of high purity tank argon was maintained in the furnace during melting.

To start melting, an arc was struck between the electrode and a pile of purified iron flakes at the bottom of the crucible. Thereafter, the arc potential was maintained at 35 to 55 v with an arc current from 700 to 1000 amp. Direct current was used with the electrode negative and the melt positive so that most of the heat would enter the melt. The melting rate was about 2 lb per min. The ingots had a maximum diameter of 5¼ in. at the bottom with a taper of ⅛ in. diam per in. of height. They weighed from 15 to 21 lb.

Table II. Nonmetallic Impurities in High Purity Iron from Several Sources

Impurity	Electrolytic* Iron	Vacuum† Metals Corp. Iron, Ferrovac E	National‡ Physical Laboratory Iron	Iron Purified in This Work: Ingot A9855, First Batch	Iron Purified in This Work: Ingot B254, Second Batch
Oxygen	0.070	0.01 max	0.001 to 0.003	0.0024	0.0010
Carbon	0.018	0.01 max	0.002 to 0.006	0.005	0.004
Nitrogen	—	<0.0002**	0.001 to 0.003	0.0001	<0.00009
Hydrogen	—	0.0002 max	<0.000005	0.00001	0.000025
Sulphur	0.004	0.003 max	0.003 to 0.005	<0.001	<0.001

* Typical analysis, according to the vendor, Plastics Metals Div., National Radiator Co. Data dated Jan. 16, 1953.
† The analyses are from a technical data sheet of the Vacuum Metals Corp., undated, but distributed in December 1953.
‡ The analyses are from refs. 3 and 4.
** This nitrogen value is specified for Ferrovac-R. Values were not published for Ferrovac-E but they are probably similar.

Fabrication of Ingots

In order to prepare stock of useful size, most of the ingots were forged at 1400°F into bars 3⅛ in. sq. The forged bars were annealed by heating to 1750°F for a few minutes and slowly cooling to eliminate the hardening caused by low temperature forging. For this anneal, several bars were packed into a gas-tight tube filled with argon and containing titanium turnings as a "getter." The BHN of as-cast ingots and annealed bars ranged from 46 to 50 as measured with a 500 kg load.

The surfaces of the annealed bars were machined to 3x3 in. and slabs cut off to make final specimens about ½ in. thick. The slabs were surface ground and electrolytically polished to remove imbedded material resulting from grinding. The polishing was carried out in such a manner that no hydrogen was introduced, but the surfaces were discolored. Buffing was followed by electrolytic cleaning, after which the bright samples were covered with a strippable lacquer and stored.

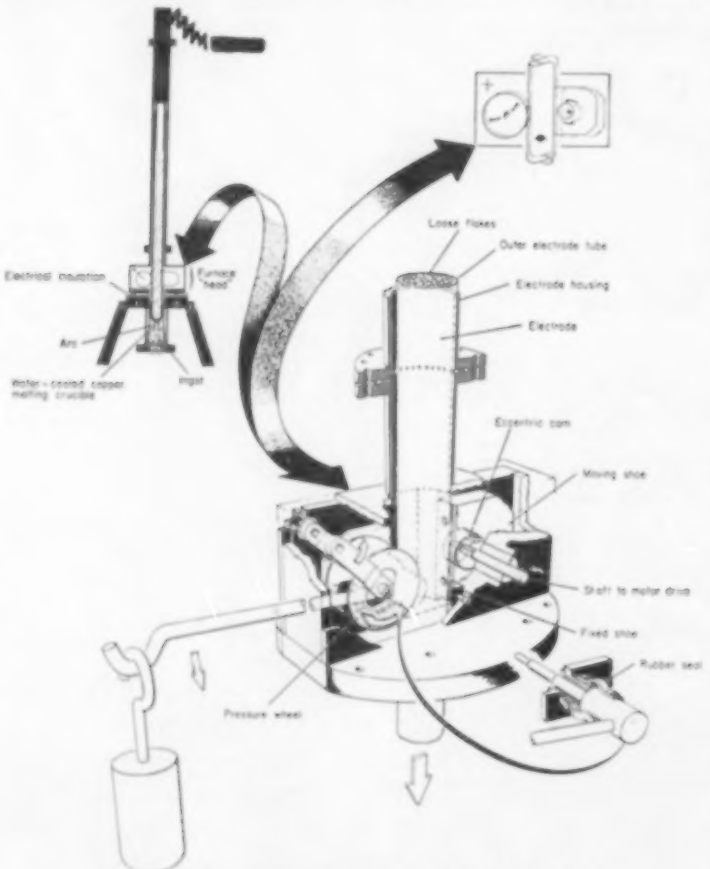

Fig. 6—Electrode drive mechanism and electrical contact.

Discussion of Results

Table I lists the chemical composition of the ingots prepared in the two batches. Some of the analyses were made on as-cast ingots, others on ingots which had been forged and annealed. The analyses are quite consistent except for two ingots which were contaminated by a water leak in the arc-melting furnace.

A special sampling technique was used for carbon analyses. Turnings gave occasional erratic values even when they were prepared with considerable care. Analyses, therefore, were made on 1 g cubes cut from the iron with a hacksaw, smoothed with a file, and cleaned in a warm 30 to 50 pct solution of HCl until the surfaces became dull. The cubes were then washed thoroughly and dried. The HCl treatment generally required more than ½ hr because high purity iron dissolves slowly.

Table II compares the nonmetallic impurity content of iron produced in this work with high purity iron from several other sources. Of special interest are the low oxygen and nitrogen contents of this iron.

Table III shows the metallic impurities found in each of the two batches. Analyses of normal electrolytic iron and of several other high purity irons are listed for comparison.

As stated previously, the purification process described here is not capable of removing metallic impurities even though it is very effective on nonmetallic impurities. There are, however, several methods for removing metallic impurities. Some of these, like the nitrate process of the Bureau of Standards,[5,6] produce electrolytic iron as an intermediate step before the nonmetallic impurities are removed. Such processes could well be combined with the hydrogen-reduction process described here to produce iron of very high purity on a large scale. The ether-separation process, also developed at the Bureau of Standards,[7] has produced iron of extremely high purity (probably the purest ever made with regard to metallic contaminants). This process also might well be a desirable means for preparing iron low in metallic impurities to serve as starting material for the present process.

Acknowledgments

The authors wish to thank the many members of the staff of Battelle Memorial Institute who helped in the preparation of high purity iron, especially C. T. Greenidge, who supervised the work and made many valuable suggestions. The project was sponsored by the American Iron and Steel Institute. Members of the subcommittee for the preparation of high purity iron were J. W. Halley, C. R. Taylor, and J. M. Hodge.

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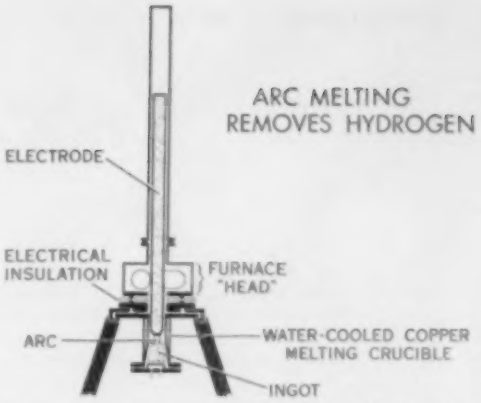

Fig. 7—Arc furnace for melting purified consumable electrodes.

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Table III. Metallic Impurities in High Purity Iron from Several Sources

Impurity	Vacuum* Metals Corp. Iron, Ferrovac E	National† Physical Laboratory Iron	Electrolytic‡ Iron	Iron Purified in this Work	
				Ingot A9555, First Batch	Ingot B254, Second Batch
Aluminum	0.001 max	0.002 or less	0.002	0.003	0.002
Antimony	—	—	—	0.001	<0.001 (not detected)
Arsenic	0.0005 max	—	Nil	0.005	<0.001 (not detected)
Beryllium	—	—	—	<0.0005 (not detected)	<0.0005 (not detected)
Boron	—	—	—	<0.0005	<0.0005
Calcium	—	—	—	0.0001	0.0001
Cadmium	—	—	—	<0.005 (not detected)	0.005 (not detected)
Chromium	0.001 max	0.002 or less	0.002	0.0005	0.001
Cobalt	0.001 max	—	0.007	0.002	0.004
Copper	0.001 max	0.007 or less	0.008	0.005	0.0008
Gallium	—	—	—	<0.005 (not detected)	<0.005 (not detected)
Lead	0.001 max	—	Nil	0.005	0.0001
Magnesium	—	—	—	0.0002	0.0002
Manganese	0.001 max	0.008 or less	0.002	0.0008	0.0004
Mercury	—	—	Nil	—	—
Molybdenum	—	—	0.002	0.001	0.001
Nickel	0.015 max	0.007 or less	0.008	0.001	0.002
Phosphorus	0.001 max	0.001 or less	0.005	0.0016	0.0007
Silicon	0.01 max	0.010 or less	0.005	0.001	0.001
Tin	0.001 max	—	0.009	0.001	0.0005
Tungsten	—	—	—	<0.001 (not detected)	<0.001 (not detected)
Vanadium	—	—	0.003	0.0004	0.0002

* The analyses are from a technical data sheet of the Vacuum Metals Corp., undated, but distributed in December 1953.
† The analyses are from ref. 3.
‡ Typical analysis, according to the vendor, Plastic Metals Div., National Radiator Co., data dated Jan. 16, 1953.

approach equilibrium. In the case being considered they contained only carbon and hydrogen. If the

A Thermodynamic Study

Fuming of Zinc from Lead Blast Furnace Slag

by R. C. Bell, G. H. Turner, and E. Peters

Zinc oxide activities in a typical lead blast furnace slag have been calculated from plant operating data. These activities were used to assess the probable effect of fuel composition, oxygen enrichment, and air preheating on the efficiency and capacity of the slag-fuming operation.

THE physical chemistry of zinc fuming has been examined with three objectives in mind: 1—to predict conditions favorable to increasing furnace capacity, 2—to predict the changes required to fume zinc more economically, and 3—to explain reported differences in the efficiencies of various slag-fuming plants.

This study, made at Trail in the plants and laboratories of The Consolidated Mining and Smelting Co. of Canada Ltd., developed from a program undertaken some three years ago on behalf of the AIME Extractive Metallurgy Div. subcommittee on slag fuming.

Lead metallurgists first became interested in the recovery of zinc from lead blast furnace slags in 1905 and 1906. An excellent review of the early experimental work has been made by Courtney,[1] who described blast furnace, reverberatory furnace, and converter methods of fuming zinc from slag. Some of the investigators did not appreciate the importance of reducing the zinc oxide content of the slag to metal in order to fume it, since they tried compressed air blast without fuel in their earliest attempts. However, by 1908, the importance of reducing the zinc was established.[2] In 1925, the Waelz process for the recovery of zinc oxide from oxidized zinc ores was developed in Germany.[3] This process was not readily adaptable to lead blast furnace slags because of the difficulty in handling fusible charges in a kiln. What appears to have been the first slag-fuming operation as it is known was commenced by the Anaconda Copper Mining Co. at East Helena, Mont. in 1927.[4] The first Trail furnace was completed in 1930, and this was followed by the construction of several other slag-fuming plants.

During the period in which slag fuming has been extensively employed, little development of the chemistry of this process as a whole has taken place. Several good papers on the petrography of lead blast furnace slags have been published,[4,5] but these studies could do little more than establish the forms in which lead and zinc occur in the initial charge and final products of the slag-fuming operation. In recent years, zinc-smelting problems have been approached from a thermodynamic point of view. Maier has published an excellent thermodynamic treatment of zinc smelting.[6] The important thermodynamic properties of zinc and its compounds have been determined and checked by other investigators.[7] However, to the best of the authors' knowledge, no thermodynamic treatment of the fuming of zinc from slag has been published.

A thermodynamic study of any process requires that the essential chemistry of that process be known. In slag fuming there appear to be some differences of opinion as to whether the active reducing agent is elemental carbon or carbon monoxide. Furthermore, some observers have noted that high volatile coals appear to be more efficient than low volatile coals, indicating that hydrogen is also an important factor in the reducing efficiency of a fuel. That both hydrogen and carbon monoxide are effective reducing agents for the zinc oxide content of lead blast furnace slags can be demonstrated readily by introducing these gases into a slag bath held in a neutral vessel at 2100°F (1150°C). Elemental carbon also will reduce zinc oxide, but it is improbable that much free carbon is available for reduction of zinc, as the reaction between the finely powdered coal and air should be largely completed before the solid coal particles reach the slag. Some large-scale fuming experiments using gaseous hydrocarbons have been carried out by other investigators, but, as far as is known, these have not been developed yet into operating processes.

The thermodynamic treatment in this paper is based on the following reactions: 1—to supply the thermal requirements

$$C + \tfrac{1}{2} O_2 \rightarrow CO \qquad [1]$$

$$C + O_2 \rightarrow CO_2 \qquad [2]$$

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \qquad [3]$$

and 2—to reduce ZnO

$$ZnO + CO \rightleftharpoons Zn + CO_2 \qquad [4]$$

$$ZnO + H_2 \rightleftharpoons Zn + H_2O. \qquad [5]$$

The furnace-gas composition also is controlled by the equilibrium constant of the familiar water-gas reaction

$$H_2O + CO \rightleftharpoons CO_2 + H_2. \qquad [6]$$

In order for the thermodynamic calculations to be quantitatively applicable, it is necessary that the chemical reactions to which they are being applied

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approach equilibrium. In the case being considered, it is necessary that the gas mixture leaving the slag bath be in equilibrium with the ZnO content of the slag. Evidence will be presented that equilibrium is attained or approached closely in the standard slag-fuming furnace. Elemental carbon reaching the slag in the vicinity of the tuyeres will reduce zinc by the reaction

$$ZnO + C \rightleftharpoons CO + Zn. \qquad [7]$$

However, if equilibrium is reached by the time the gases leave the slag surface, this intermediate reaction should be of little importance to the overall result.

In addition to the main reactions involving the reduction of the oxidized zinc content of the Fe-Zn-Ca silicate slag to zinc metal by carbon monoxide and hydrogen, a number of less important reactions occur simultaneously. Lead is believed to be largely volatilized as the sulphide, and a small amount of zinc also may be assumed to leave the slag in this form. A variety of minor metals are fumed out also but there is little direct evidence of the form in which they are removed. It is known, however, that most of the minor elements associated with lead and zinc have appreciable vapor pressures in the temperature range 2100° to 2300°F either as the metal or the sulphide. The major components of the slag, lime, iron, silica, alumina, and sulphur, are known to affect the rate at which zinc is fumed.

An important feature of the slag-fuming process is the use of the fuel both as a source of heat and as a chemical reducing agent. Carbon and hydrogen compete for oxygen from both zinc oxide and the air, reactions 4 and 5 absorbing heat and reactions 1, 2, and 3 evolving heat. The active reducing agent is that part of the CO and H_2 remaining after the heat requirements have been met. If the demands upon the heat requirements could be lessened by enriching the air blast with oxygen or by preheating the air, more CO and H_2 would be available for reduction. The use of oxygen-enriched air at the Trail slag-fuming plant a few years ago provided some experimental data with which these calculations can be compared.

In summary, the detailed objectives of this study are then: 1—to examine the effect of varying the C-H ratio of the fuel over a wide range, upon the probable efficiency of the process in terms of weight of zinc fumed per unit weight of fuel, and also the effect upon furnace capacity; and 2—to explore the conflicting requirements of using the fuel both as a reducing agent and as a source of heat.

Zinc Oxide Activity in Lead Blast Furnace Slags

In order to calculate the effect of changes in fuel and other process and operational conditions, it was necessary to know the equilibrium constants of reactions 4, 5, and 6 in the required temperature range and the zinc oxide activities in the slag-composition range used in the slag-fuming process. The equilibrium constants were available, but the zinc oxide-activity data were not. It was decided to calculate zinc oxide activities from carefully controlled zinc-elimination runs made in the No. 2 slag-fuming furnace of the Trail Smelter. The method of treating the data follows:

The process is started with one unit of fuel which is defined as the amount of fuel that requires 1 lb mol of oxygen (32 lb O_2) for complete combustion. At this stage, the fuels will be treated as though they contained only carbon and hydrogen. If the fuel contains (a) mol of carbon per unit, the hydrogen content will be $2(1-a)$ mol. Let the coal-air mixture be such that the oxygen input is (b) mol, and the nitrogen input associated with the oxygen is N mol. For air, $N/b = 0.79/0.21$. This ratio would be decreased by enriching the air with oxygen.

The gas mixture passing through the slag will consist essentially of six components, Zn, N_2, H_2, H_2O, CO, and CO_2. The following symbols are used to represent the molar quantity of each gas per unit of fuel at equilibrium: Zn = z, $N_2 = N$, $H_2 = x$, $H_2O = 2(1-a)-x$, CO = y, $CO_2 = a-y$, and the total = $M = 2 - a + N + z$.

To solve for the unknowns, three equations are required. The first equation represents an oxygen balance. All the oxygen entering the tuyeres is converted to H_2O, CO, and CO_2. In addition, some of the oxygen found in these gases originated as ZnO in the slag. The oxygen balance is

$$b + \frac{z}{2} = \frac{2(1-a)-x}{2} + \frac{y}{2} + (a-y)$$

which simplifies to

$$x + y + z = 2(1-b). \qquad [8]$$

A second equation can be obtained from the equilibrium of reaction 4

$$CO + ZnO \rightleftharpoons CO_2 + Zn$$

$$K_4 = \frac{P_{CO_2} \cdot P_{Zn}}{P_{CO} \cdot A_{ZnO}}$$

where P represents the partial pressure of the gaseous components, A_{ZnO} the activity of ZnO in the slag, and K_4 the equilibrium constant of this reaction. To convert the unknowns from the units of mol per unit of fuel to partial pressures, the total number of mols must be divided by M

$$K_4 = \frac{(a-y/M) \cdot z/M}{y/M \cdot A_{ZnO}}.$$

Therefore,

$$A_{ZnO} \cdot K_4 = \frac{(a-y)z}{y(2-a+N+z)}. \qquad [9]$$

The third equation may be based upon reaction 5 or 6. The latter was chosen because its equilibrium constants were available in the required temperature range.

$$K_6 = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} = \frac{(a-y)x}{y(2(1-a)-x)}. \qquad [10]$$

The equilibrium constants K_4 and K_6 have been obtained from published data[6, 8, 9] and are plotted as functions of temperature in Fig. 1.

Zinc-elimination curves were drawn from analyses of slag samples taken from the slag-fuming furnace at 10 min intervals during the blow. These curves were differentiated graphically to obtain instantaneous zinc-fuming rates from which the value of z was calculated. The other unknowns were obtained by solving the oxygen-balance Eq. 8 and the water-gas equilibrium Eq. 10. Using these values, the zinc oxide activity was then calculated from Eq. 9. This procedure was followed for three blows of different-size charges, all having a similar chemical composition. Slag charge sizes and compositions are shown in Table I.

The resulting zinc oxide activites are shown as a

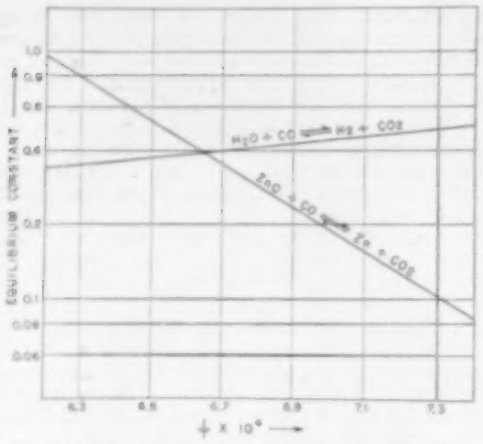

Fig. 1—Equilibrium constants as a function of temperature.

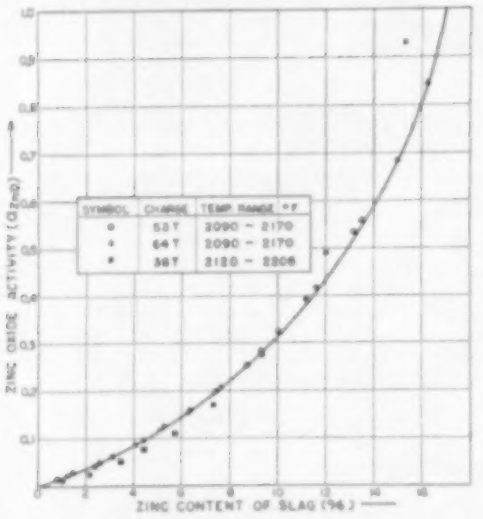

Fig. 2—The activity of zinc oxide in fuming furnace slag.

function of zinc concentration in the slag in Fig. 2. The assumption that equilibrium is attained in the slag-fuming process is supported by these results in two ways:

1—The activity-concentration relationship indicates saturation of the slag with zinc oxide at approximately 17 pct Zn, which coincides with the maximum zinc content attainable in Trail lead blast furnace slags of the foregoing composition.

2—The activity curves of the three blows agree closely with no indication that the smallest charge was below the remaining two in degree of completion. If equilibrium were not attained, the resulting activity values would have been depressed. In the case of the 36 ton charge, the opposite appears to have been true.

All calculations have been made for slags of the Trail type, but it is reasonable to expect that variations in slag composition will not alter the general nature of the activity-concentration relationship.

Influence of Fuel Composition on Zinc-Fuming Rates

For a given zinc oxide activity, fuel and air-input rate, and temperature, the equilibrium amounts of

Table I. Data on Experimental Slag-Fuming Runs

Charge, Tons	Approximate Depth of Slag, In.	Pb	Zn	CaO	SiO_2	Al_2O_3	Fe
36	29	1.9	15.2	9.0	22.5	6.4	28.6
53	30	1.8	14.3	9.0	22.6	6.0	28.7
64	40	1.8	16.2	9.0	20.3	5.1	28.8

zinc, carbon monoxide, and hydrogen in the gas phase may be calculated by simultaneous solution of the Eqs. 8, 9, and 10. The nitrogen in the mixture is obtainable from the air-blast rate, and the carbon dioxide and water concentrations follow from a C-H material balance. The gas composition was determined for a range of fuel-air ratios corresponding with combustions of 50 to 100 pct. The percentage of combustion is a measure of the amount of oxygen supplied per unit of fuel, 100 pct combustion indicating that a stoichiometric amount of oxygen is provided for complete combustion of the fuel to carbon dioxide and water.

No actual experimental data are available with which to compare these calculated gas compositions. It is planned to make such measurements in the Trail furnace when the opportunity arises.

Calculations were made for initial and final conditions in the furnace operation, i.e., for zinc oxide activities of 1.00 to 0.04 (representing 17 and 2 pct Zn in the slag, respectively, as seen in Fig. 2) for a variety of fuels, fuel-air ratios, and blast-air conditions. The temperatures 2090° and 2200°F were chosen as the initial and final slag temperatures in accordance with typical operation of the No. 2 fuming furnace at Trail.

Heat Balance for the Fuming Operation: A most important consideration is to ensure that sufficient heat be available to maintain the fuming-furnace charge within the above temperature range. A heat balance incorporating the heats of the exothermic combustion reactions and the endothermic zinc oxide-reduction reactions, as well as the latent and sensible heats of the components of the equilibrium gas mixture, was used for calculating the heat requirements to provide for furnace-heat losses. These requirements, which include radiation losses and heat given up to cooling water, were obtained for a number of hypothetical fuels containing carbon and hydrogen in varying proportion. Fig. 3 shows the relationship between this excess reaction heat and the percentage of combustion of two such fuels, whose compositions are representative of a medium volatile coal and natural gas (methane). Practical heating values have been used, rather than the heats of combustion of carbon and hydrogen in their standard states, for preparing these curves.

The excess heat available to provide for furnace losses at the beginning and end of a blow was calculated to be about 18,900 and 30,960 Btu, respectively, which values are shown as horizontal lines in Fig. 3. The main reason for the difference in these values is the decreasing heat requirements of the endothermic zinc oxide-reduction reactions as the blow proceeds. The difference goes into raising the temperature of the slag bath and in meeting the consequently higher heat losses. Since these requirements must be met to control the slag temperature within the operating range, the intersection of the excess heat lines with the constant heat lines determines the percentage of combustion at which the furnace must operate, for a specific fuel and grade of blast air. For

each set of fuel conditions, a percentage of combustion can be chosen to satisfy the heat requirements.

The calculated excess heats, as given previously, agree very closely with actual measured heat losses to the cooling water for the Trail furnace.

If auxiliary heat is supplied, the constant heat lines can be set at a correspondingly lower level, permitting operation at a lower percentage of combustion. This permits a higher zinc-elimination rate, as can be seen from Fig. 4.

Zinc Elimination Curves: The zinc-fuming rate for any fuel and air-input rate and any zinc oxide activity may be calculated by solving Eqs. 8, 9, and 10, as has been described. Fig. 4, obtained for the same conditions as used in preparing Fig. 3, shows the rates of zinc elimination at the beginning and end of a blow for a medium volatile coal and pure methane.

In order to integrate the initial and final fuming rates into an elimination curve giving the fuming rates throughout the blow, a standard formula was chosen

$$\log_{10} (\text{pct Zn}) = A - Bt - Ct^2$$

where (pct Zn) is the percentage of zinc in the slag at time t, and A, B, and C are constants fixed by the initial zinc concentration and the terminal rates of fuming.

The best test for the usefulness of this procedure is a comparison of the elimination curves obtained by these calculations and curves obtained from plant data. Such a comparison is made in the logarithmic plots of Fig. 5. Excellent agreement between the curves is noted throughout most of the fuming operation. The small deviation towards the end of the blow can be attributed to slight differences in the conditions of the theoretical and experimental blows.

Effect of Hydrogen Content of the Fuel: Although coal is being used in all regular zinc-fuming furnaces, the use of other fuels, particularly natural gas, has been considered for this process. Calculations have been made for a range of fuels from pure carbon to hydrogen, including low and high volatile coals, fuel oil, and natural gas. For the sake of simplicity, fuels have been considered only in terms of their hydrogen and carbon contents. The zinc-elimination curves for certain fuels are shown in Fig. 6.

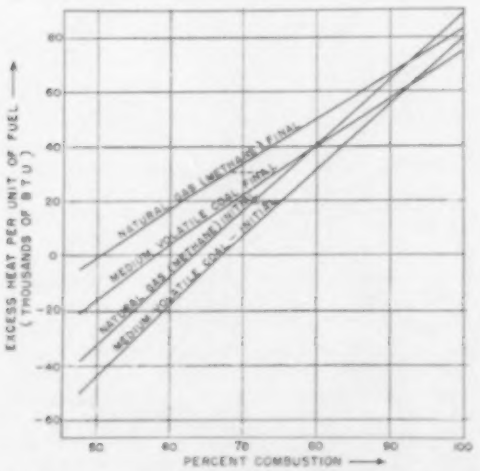
EXCESS HEAT PER UNIT OF FUEL (THOUSANDS OF B T U)
PERCENT COMBUSTION
NATURAL GAS (METHANE) FINAL
MEDIUM VOLATILE COAL FINAL
NATURAL GAS (METHANE) INITIAL
MEDIUM VOLATILE COAL INITIAL

Fig. 3—Excess reaction heats for medium volatile coal and natural gas (methane).

These curves show that zinc-fuming rates increase with increasing hydrogen content of the fuel. Even a change from a medium volatile to a high volatile coal will offer some improvement, in agreement with some reported observations.

Separation of the Heating and Reducing Functions of the Fuel-Air Mixture

In conventional zinc fuming, the heat producing and zinc-reducing functions are both fulfilled at the same time. These functions could be partially separated by burning one bank of tuyeres at a higher percentage of combustion than normal and another bank at a lower percentage of combustion. The average of the two banks of tuyeres then would be at the equivalent of normal operation.

This situation will result in nearly the same excess reaction heat, since excess reaction heats are almost a linear function of the percentage of combustion as indicated in Fig. 3. However, the zinc-elimination rate will be increased. The average of the two operations will lie on a chord drawn through the curves in Fig. 4 combining the two sets of conditions, and this chord lies distinctly above the main part of the curve in the case of coal. The actual zinc-elimination

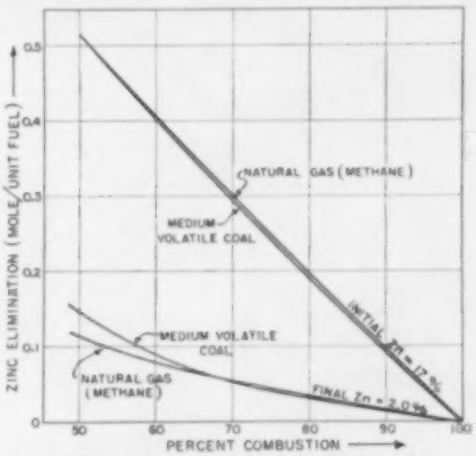

Fig. 4—Zinc-production rates for medium volatile coal and natural gas (methane).

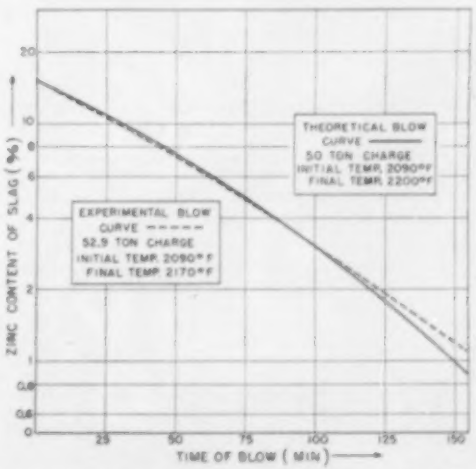

Fig. 5—Comparison of theoretically determined and experimental zinc-elimination curves.

curve was calculated for conditions of 55 and 95 pct combustion of medium volatile coal at the tuyeres and is compared with a calculated curve representing uniform operation at 75 pct combustion in Fig. 7.

Effect of Reducing Thermal Requirements of the Furnace on Zinc-Fuming Rates

Two methods have been used for increasing the effective heat output of an operation such as the one being considered: 1—oxygen enrichment and 2—preheating of the blast air. Both of these methods have been examined in this study.

Oxygen Enrichment: The effect of oxygen enrichment is to allow a substantial increase in fuel input without increasing the burden of inert nitrogen entering the furnace. A lower percentage of combustion then may be attained with a corresponding increase in the concentration of zinc in the furnace gases. The authors' calculations were carried out for the enrichment of a 17,000 cfm blast-air stream with 1,000 cfm O_2 raising the oxygen content of the total to 25.6 pct. The use of oxygen-enriched air in slag fuming at the Trail Smelter was reported several years ago.[7] The increase in fuming rate predicted by

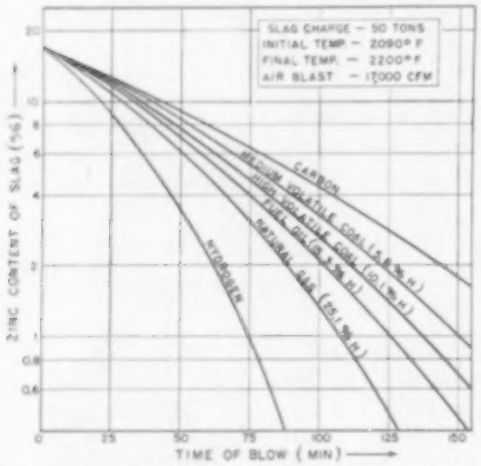
SLAG CHARGE — 50 TONS
INITIAL TEMP. — 2090° F
FINAL TEMP. — 2200° F
AIR BLAST — 17000 CFM
CARBON
MEDIUM VOLATILE COAL (5.8 % H)
HIGH VOLATILE COAL (6.1 % H)
FUEL OIL (9.3 % H)
NATURAL GAS (25 % H)
HYDROGEN
ZINC CONTENT OF SLAG (%)
TIME OF BLOW (MIN)

Fig. 6—Comparison of theoretical zinc-elimination curves for various fuels.

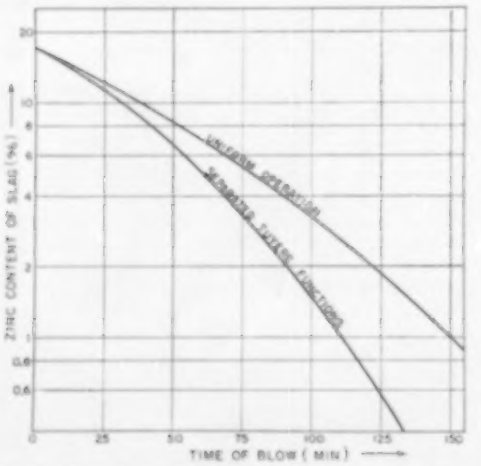

Fig. 7—Effect of separating the heating and reducing functions of the coal-air mixtures.

Table II. Calculated Increases in Zinc-Fuming Rates by Various Process Changes: Slag Charge, 50 Tons; Zn Recovery, 90 Pct; Air Blast, 17,000 Cfm

Method	Conditions	Approximate Increase in Fuming Capacity, Pct	Fuel (Consumption), Lb/Lb Zn
Carbon	Normal	−15	1.4
Medium volatile coal	Normal	0	1.6
High volatile coal	Normal	10	1.15
Heavy fuel oil	Normal	20	0.95
Natural gas (CH_4)	Normal	37	0.79
Hydrogen	Normal	100	0.25
Oxygen-enriched blast	Medium volatile coal 25.6 pct O_2 in blast air	60	1.37
Preheated blast	Medium volatile coal blast air at 1000°F	80	0.95
Separation of heating and reducing functions	Gas stream alternating between 55 and 95 pct combustion	35	1.3

the present calculations, shown in Fig. 8, agrees well with that observed in the plant trials.

Preheating the Blast Air: The calculated effects of preheating the blast air to 1,000°F are also shown in Fig. 8. Similar to the treatment used for oxygen enrichment, any addition of external heat will allow a decrease in the percentage of combustion, obtained in this case by increasing the fuel fed to the furnace.

Discussion

The authors' calculations, results of which are summarized in Table II, indicate the possibility of substantial improvements in slag-fuming furnace performance. Combining several of the suggested methods of increasing the capacity or fuel efficiency should yield a combined increase in zinc-fuming rates, which could be calculated by the method outlined. However, this can only be achieved in practice if chemical equilibrium is maintained in the reaction system.

These calculations can account, in part, for the variations in slag-fuming efficiency known to exist among the slag-fuming furnaces now in operation. The predicted improvement in slag-fuming rate by oxygen enrichment is in agreement with that observed in practice. It is known that some attempts to use gaseous fuels in slag fuming have been made and that results have not been encouraging. One factor which may affect the use of gaseous fuels in the conventional furnace is the ability of the reaction to

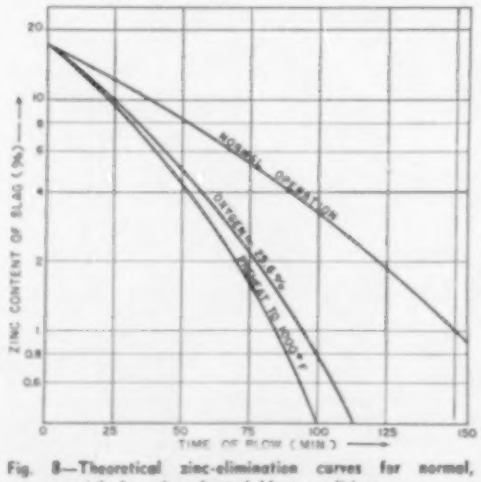

Fig. 8—Theoretical zinc-elimination curves for normal, oxygen-enriched, and preheated blast conditions.

reach equilibrium. Some metallurgists feel that solid carbon particles are essential to the rapid fuming of zinc from slag, if for no other reason than to maintain a very large area of contact between reducing gas and slag. Such a condition will favor, in effect, the attainment of equilibrium in the slag bath.

It is hoped that the methods described in this report may be of use to others interested in estimating the probable results of contemplated changes in the slag-fuming process.

Discussion of this paper, if any, will appear in JOURNAL OF METALS, November 1955, and in AIME Metals Branch *Transactions*, Vol. **203**, 1955.

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Solubility of Oxygen in Liquid Nickel and Fe-Ni Alloys

by Henry A. Wriedt and John Chipman

DURING the past twenty years, a considerable background of knowledge has been built up on the chemical behavior of oxygen in liquid iron. Little is known regarding oxygen in liquid nickel or the effect of nickel as an alloying element on the behavior of oxygen in liquid steel.

The solubility of oxygen in liquid iron was determined by Fetters and Chipman[1] and, more precisely, by Taylor and Chipman.[2] The Ni-NiO eutectic was placed by Merica and Waltenberg[3, 4] at 1438°C and 0.24 pct O, and this point has been confirmed by others.[5, 6] It was reported by von Bohlen und Halbach and Leitgebel[7] that nickel and its oxide are miscible in all proportions at 1600°C, but this report is discredited by observations of others. The melting point of NiO according to von Wartenberg and Reusch[8] is 1990°C. Approximate values of oxygen solubility at several temperatures were reported by Hensel and Scott.[9] The data of Krupowski and Balicki[10] are inconsistent with those of Hensel and Scott and indicate a solubility less than half that found in the present study.

For oxygen solubility in Fe-Ni alloys under pure iron oxide-nickel oxide slags, only the scattered data of von Bohlen und Halbach and Leitgebel[7] are available. The careful work of Bardenheuer and Brauns[11] involved silica-saturated slags. The equilibrium between Fe-Ni alloys and iron oxide-nickel oxide slags was studied by zur Strassen[12] and by Jander and Senf,[13] but no oxygen analyses were reported.

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Oxygen in Pure Nickel

Apparatus and Method: Samples were taken with a "Taylor sampler" from a bath of molten electrolytic nickel held under an air atmosphere in a magnesia-lined 30 lb induction furnace. Saturation of the melt with oxygen was effected partly by the addition of chemically pure black nickel oxide and partly by the air atmosphere. Samples were taken only when there was a clearly visible oxide phase present. To avoid contamination of this oxide phase, the silica-sheathed Pt—Pt-10 pct Rh thermocouples, by means of which temperatures were measured, were immersed in the melt for the minimum time consistent with accurate reading. Samples and temperature readings were taken only after the furnace had been

Table I. Oxygen Solubility in Liquid Nickel

Sample No.	Temperature, °C	Oxygen Analysis	
		Wt Pct	Mol Pct
S-1	1622	0.878	3.14
S-3	1641	0.778	2.79
S-5	1560	0.562	2.03
S-6	1527	0.468	1.70
S-7	1550	0.628	2.26
S-8	1545	0.533	1.93
S-9	1601	1.63	5.73
SS-1	1450	0.294	1.07
SS-2	1501	0.422	1.53
SS-3	1550	0.646	2.34

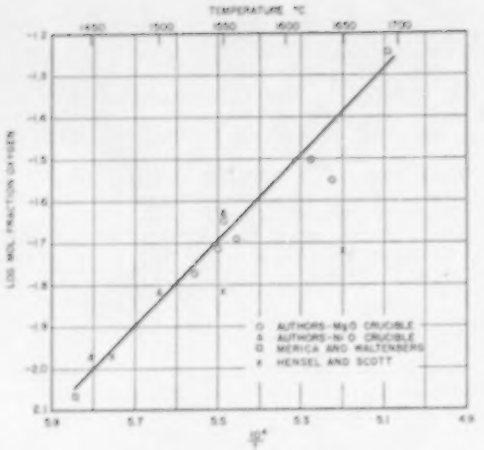

Fig. 1—Experimental data on oxygen solubility in liquid nickel.

at a fixed power setting for at least ¼ hr and, in many cases, to check the temperature constancy, temperature readings were taken both immediately before and after the sampling. Samples S1 to S9 of Table I were obtained in this way.

The remaining three data points of Table I were obtained from runs in a globar-element vertical tube furnace using an argon atmosphere. In each case, the oxide in contact with the metal was pure nickel oxide. To effect this condition, the metal was held in an alumina crucible which had a thick inner lining of nickel oxide. The excess nickel oxide was found after each run to have sintered and contracted away from the alumina shell, except at a few points of support, and the metal was held in this sintered cup. Each 7 to 10 g sample was held at temperature at least 2 hr in the temperature-controlled furnace. The Pt—Pt-10 pct Rh thermocouples were located adjacent to the crucible in the constant temperature zone of the furnace. At the end of each run, the melt and crucible were quickly quenched in mercury.

Samples were analyzed for oxygen by a standard

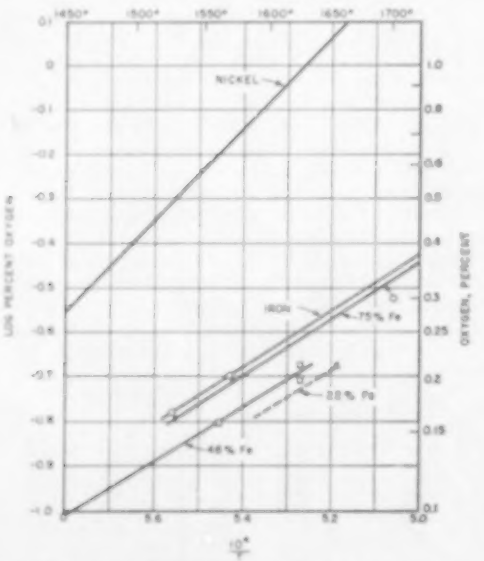

Fig. 2—Solubility of oxygen in liquid nickel, iron, and alloys.

Table II. Oxygen Solubility in Alloys (30 Lb Furnace, Magnesia Crucible)

Sample No.	Temperature, °C	Analysis,* Wt Pct	
		Fe†	O
SSS-1	1655	22.2	0.210
SSS-2	1651	48.1	0.097
SSS-3	1561	48.2	0.158
SSS-4	1625	48.0	0.196
SSS-5	1625	48.0	0.213
SSS-6	1536	75.3	0.166
SSS-7	1569	75.1	0.202
SSS-8	1705	75.0	0.302

* Nitrogen content of all samples was <0.003 pct.
† By difference.

vacuum fusion method. No attempt was made to determine the exact compositions of oxide phases in equilibrium with melts.

Results: The data have been plotted as log mol fraction oxygen vs reciprocal of absolute temperature in Fig. 1. Also included in this plot are the eutectic point of the Ni-Ni oxide system, as given by Merica and Waltenberg,[4] and three points given by Hensel and Scott.[5]

With the exception of one point of the authors' and two of Hensel and Scott, the data can all be fitted by a line given by the expression

$$\log \text{mol fraction } \underline{O} = -10{,}270/T + 3.95.$$

Expressed in weight percent, this is equivalent to

$$\log \text{Pct } \underline{O} = -10{,}270/T + 5.40.$$

The heat of solution of solid nickel oxide in liquid nickel is +47 kcal.

It will be observed from Fig. 1 that the solubility of oxygen is apparently slightly higher in those cases where the only oxide phase was pure nickel oxide. However, in view of the small difference involved, it was felt that separate treatment for the two sets of data was hardly justified. The authors' one point which falls markedly low was for a sample taken soon after a nickel metal addition to the bath and may not represent a saturation point. The reason for the large departure from the line by the two points of Hensel and Scott may be loss of precipitated oxide during cooling or analytical errors inherent in the aluminum-deoxidation method of analysis.

Oxygen in Fe-Ni Alloys

Apparatus and Method: A melt was made in a magnesia-lined, 30 lb induction furnace and samples were taken with Taylor samplers. The technique was similar to that described in the preceding section with the following differences: A prepurified nitrogen atmosphere was used to avoid uncontrolled atmospheric oxidation which would have removed iron preferentially from the alloys. Ferric oxide was used as a source of oxygen. Electrolytic iron additions were made during the run to obtain three different alloy compositions, viz., 22.2, 48.1, and 75.1 pct Fe.

Several slag samples were obtained from baths containing 48 and 75 pct Fe. These were found to contain 90 to 92 pct FeO (based on total iron), 1 to 2 pct SiO_2, 2 to 4 pct MgO, and 0.4 to 1.2 pct NiO.

With this furnace arrangement it was found difficult to set the melt temperature exactly at the desired value of 1594°C. Therefore, samples were taken at three arbitrary temperatures for the 48.1 and 75.1 pct Fe alloys and the desired saturation limits at 1594°C were interpolated from the results of these. The data are given in Table II.

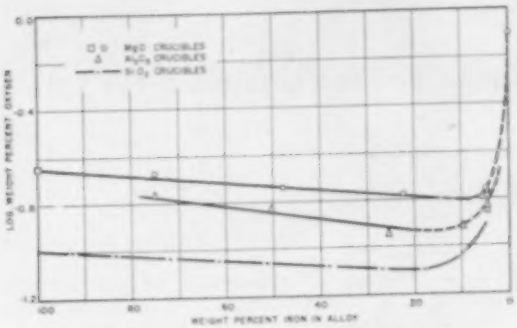

Fig. 3—Solubility of oxygen in Fe-Ni alloys at 1594°C.

A number of points were obtained directly at 1594°C using an apparatus which had been used for studies of gas-metal equilibria. A charge of 35 g of metal, heated by induction, was held in the furnace chamber under an atmosphere of argon. Oxygen in excess of the quantity required for saturation was supplied as iron oxide or by introduction of water vapor-hydrogen mixtures having oxygen activities greater than those of the respective oxygen-saturated alloys. The temperature of the melt was measured by means of an optical pyrometer sighted on the metal surface through a prism and window in the furnace head. The charge, the temperature of which was set by manual control of the power unit, was quenched by a blast of cold helium at the conclusion of a run. Runs were made in this apparatus using both magnesia and alumina crucibles. The data are shown in Table III.

Results: The data from the 30 lb magnesia-lined induction furnace (Table II) are plotted as log wt pct O vs reciprocal of absolute temperature in Fig. 2. The solubility in pure nickel and the line determined for pure iron by Taylor and Chipman[2] are shown for comparison.

The experimental data at 48.1 pct Fe appear quite reasonable, indicating a heat of solution of the oxide of +28 kcal in good agreement with 28.9 kcal for pure iron. The data for 75.1 pct Fe are less satisfactory. A line of best fit for these three points would indicate a markedly lower heat of solution for the oxide than those established in the cases of pure iron and 48.1 pct Fe. Since there is no reason to believe that such an anomaly exists, a line has been drawn in Fig. 2 whose slope is the same as that for the pure iron line but whose position was fixed from equal weighting of the data points.

The interpolated solubility points at 1594°C from the previous data, together with a point calculated for 22.2 pct Fe using a heat of solution of +28 kcal and the datum point at 1655°C, are plotted in Fig. 3 together with the data points obtained from those runs made in the 35 g induction furnace using magnesia crucibles. Taylor and Chipman's point for pure iron and the authors' point for pure nickel are shown. The section of the curve below 5 pct Fe is quite uncertain and, although drawn as a continuous dotted line, should exhibit a discontinuity at the point of three-phase equilibrium where liquid metal, liquid oxide, and solid oxide coexist. Experiments were not conducted to establish the position of this discontinuity, on the high nickel side of which the oxide is solid.

The data for solubility of oxygen in the presence of alumina are plotted also in Fig. 3 and, as would be expected, the curve drawn through these points lies lower than the magnesia line. This curve must be regarded as only approximate, particularly in the region below 10 pct Fe. The nature of the alumina-iron oxide phase was not determined.

A line representing the data of Bardenheuer and Brauns in silica crucibles under silica-saturated slags is included for comparison. It is evident from the position of this line that the activity of oxygen in the silica-saturated slags is less than that in the nearly pure oxides of the magnesia crucible by a substantially constant factor. The alumina-saturated slags are intermediate.

Table IV gives a summary of the data interpolated to even temperatures and concentrations.

Table III. Solubility of Oxygen in Fe-Ni Alloys at 1594°C

Crucible	Atmosphere	Fe, Wt Pct	O, Wt Pct
Al_2O_3	Argon	80.5	0.148
Al_2O_3	H_2O-H_2	4.81	0.167
Al_2O_3	H_2O-H_2	4.83	0.148
Al_2O_3	H_2O-H_2	4.87	0.142
Al_2O_3	H_2O-H_2	10.07	0.122
Al_2O_3	H_2O-H_2	25.6	0.114
Al_2O_3	H_2O-H_2	74.9	0.171
MgO	Argon	4.97	0.174
MgO	Argon	9.77	0.160

Table IV. Summary of Solubility Data (Interpolated)

Temperature, °C	Solubility, Wt Pct O			
	Ni	20 Pct Fe	50 Pct Fe	Fe
1480	0.38	—	0.10	—
1500	0.40	—	0.12	—
1550	0.56	0.13	0.15	0.18
1600	0.82	0.16	0.19	0.23
1650	1.16	0.20	0.23	0.28
1700	1.59	—	—	0.34

Acknowledgment

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Discussion of this paper, if any, will appear in JOURNAL OF METALS, November 1955, and in AIME Metals Branch *Transactions*, Vol. **203**, 1955.

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Technical Note

Elastic and Plastic Strains and Watt Losses in Grain-Oriented 3 Pct Si-Fe

by Peter W. Neurath and Robert E. Waite

INFORMATION is available on the effect of stress on permeability, coercive force, and hysteresis for a variety of materials[1] but for the technically important grain-oriented 3 pct Si-Fe[2] the stress effects are not adequately covered in the literature; in addition, most of the stress data do not permit estimation of what would happen to the 60 cycle watt losses of the material under stress. Direct measurement of these effects therefore has been made and appears to be of considerable theoretical as well as practical interest. Losses were measured on the central 25 cm portion of 40x3x0.035 cm samples which could be stressed in a small tensile machine built for this purpose. Under tension the following effects, illustrated in the figures by a particular example, were observed:

1—"Unstrained" material of commercially acceptable loss level shows no change or a small increase in loss at low elastic stresses. For the sample shown in the figures, this is illustrated during the initial run, where a 7 pct increase is observed (Fig. 1).

2—There is no additional change in loss when the sample is further strained up to the elastic limit (Fig. 1). Within that limit the loss-stress curve is reversible. This is not illustrated in Fig. 1.

3—Even in the plastic range only small increases in loss are observed as long as the sample is kept under stress (Fig. 2, point *N*); often no increase can be observed (Fig. 1).

4—A large increase in watt losses is observed after removal of the stress subsequent to plastic deformation (Figs. 1 and 2).

5—All, or nearly all, of the foregoing increase in loss due to plastic deformation can be eliminated by a reapplication of tensile stress but returns upon removal of this stress. This is illustrated in the third run (Fig. 3). This run remains within the elastic limit and shows the reversibility of the stress-loss curve under this condition.

These findings have been confirmed on large samples (approximately 200x10x0.035 cm and larger) except that under 1 no initial increase in loss was ever observed on these. The accuracy of the watt loss measurements is of the order of 1 pct.

Neither bending of the sample in the tensioning device nor a redistribution of flux along the width of the sample accounts for these results. They therefore must be explained on the basis of either a change in the domain configuration due to stress or a change in the domain wall mobility.

Acknowledgment

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[1] R. M. Bozorth: Ferromagnetism. (1951) Chap. 13. New York. D. Van Nostrand Co.

[2] R. M. Bozorth: Ferromagnetism. (1951) Chap. 13, p. 88. New York. D. Van Nostrand Co.

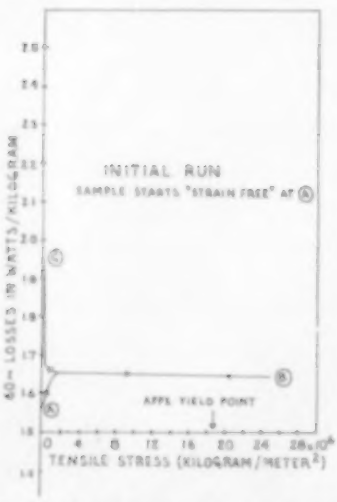

Fig. 1—Change of 60 cycle watt loss of grain-oriented 3 pct Si-Fe under tension. Losses were measured at a peak flux density of 15,500 gauss. The initially strain free sample (*A*) was stressed beyond the yield point (*B*) and, after complete release of the tension, had increased in losses (*C*).

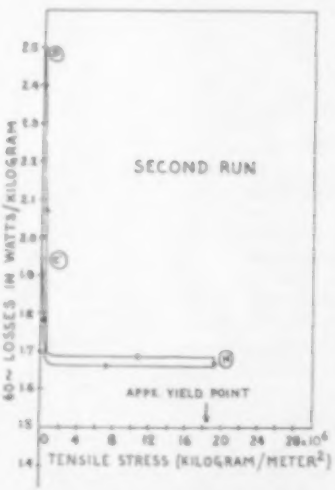

Fig. 2—A second run on the same sample as in Fig. 1. At the maximum stress *N*, Neumann bands could be heard to form. The initial point *C'* is identical with *C* of Fig. 1.

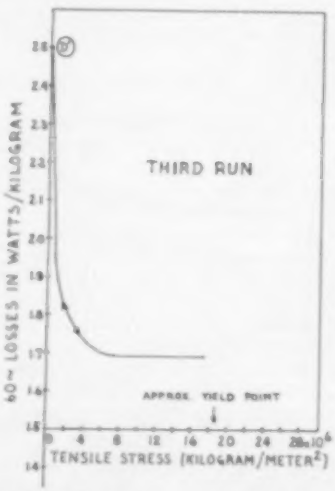

Fig. 3—A third run on the same sample as shown in Figs. 1 and 2. This run remained within the elastic limit. Its initial point *D'* is identical with *D* of Fig. 2.

Electrical Conduction in Molten Cu-Fe Sulphide Mattes

by G. M. Pound, G. Derge, and G. Osuch

Using a new alternating-current potentiometer circuit and a specially designed four-terminal cell, the specific conductance of molten Cu_2S-FeS mattes was measured as a function of temperature, from the liquidus to 1500°C, over the complete range of composition. The high conductivities, about 1500 ohm^{-1} cm^{-1} for FeS and 100 ohm^{-1} cm^{-1} for Cu_2S, indicate that the conduction is electronic rather than ionic. Molten FeS has a negative temperature coefficient of specific conductance, resembling metallic conduction. Molten Cu_2S has a positive temperature coefficient, resembling semiconduction. The binary roughly follows an additive rule of mixtures with respect to both magnitude and temperature coefficient of specific conductance. Metallic bonding in the liquid is postulated to explain these phenomena.

MUCH has been learned in the past about the nature of liquids and the ionic or molecular species in solution by means of electrical measurements. Thus, dielectric constants[1, 2] have given information about molecular liquids such as water and benzene. Measurements of dielectric constant usually are impossible in electrically conducting liquids, such as aqueous solutions of ionic salts and molten ionic salts. However, measurements of electrical conductance and ionic transference have provided much knowledge about the latter systems.[3,4]

In recent years, the ionic nature of certain molten metallurgical slags has been established by Derge and Martin[5] through electrical conductance and electrolysis measurements. Chipman, Inouye, and Tomlinson[6] have studied the electrical conductance of molten FeO and report a high specific conductance of about 200 ohm^{-1} cm^{-1} (compared with 4 ohm^{-1} cm^{-1} for an ordinary ionic liquid such as molten NaCl) and a positive temperature coefficient of conductance. They interpret these results in terms of p-type semiconduction by analogy to the situation in solid FeO.[7] Simnad and Derge[8] have studied cell efficiency in the electrolysis of molten FeO-SiO_2 systems and conclude that ordinary ionic conductance increases with SiO_2 content.

Very recently, interest has been revived in the electrical conductance of liquid metals and liquid metallic solutions. Scala and Robertson[9] report a close resemblance between the liquid and solid states with respect to thermal, structural, and compositional relationships.

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Molten sulphides have not received a great deal of attention. Bornemann and von Rauschenplat[10] measured the specific conductance of molten Cu_2S as a function of temperature with a four-terminal cell using direct current. A high specific conductance and a positive temperature coefficient were found in that investigation.[10] Using a two-electrode apparatus, Savelsberg[11] electrolyzed various molten sulphide mixtures. He concluded that pure molten Cu_2S and FeS were electronic conductors but that the mixtures exhibited some ionic conduction.

In the present investigation, the specific conductance of the industrially important Cu-Fe sulphide mattes was measured as a function of temperature and composition in order to investigate the mode of electrical conduction and the structure of these molten mattes. An alternating-current circuit was used to eliminate the effect of any possible electrode reactions.

Apparatus

The Conductance Cell: Due to the high specific conductance of the systems studied (10^2 to 10^4 ohm^{-1} cm^{-1}), the classical two-terminal cell and Wheatstone bridge apparatus could not be used. A four-terminal cell was developed in order to eliminate lead resistance, and an ac potentiometer circuit was designed to give rapid and sufficiently accurate measurements of the cell resistance. A diagram of the conductivity cell is given in Fig. 1. The molten matte is contained in a dense alundum crucible, and spectrographic graphite rods that dip into the molten matte serve as the four conductance terminals. Two of the graphite rods on opposite sides of the cell serve as current-carrying leads, and the other two graphite rods are null-current probes that detect the potential drop across the cell. These graphite rods are contained in silica tubes, and the lower constricted portions of the two silica tubes define the column of liquid whose electrical resistance is being measured. The electrical resistance of the broad ex-

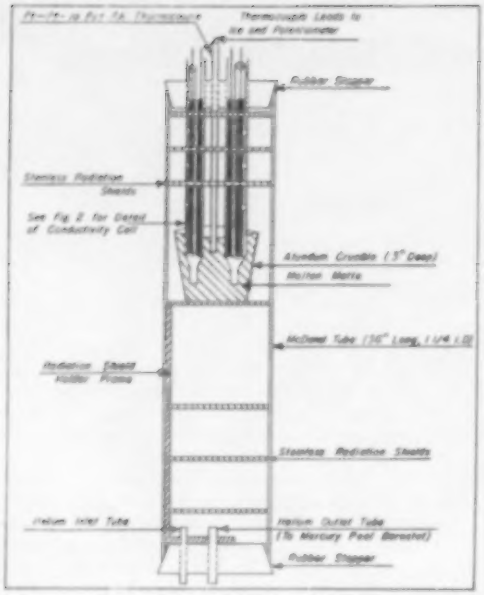

Fig. 1—Matte conductivity cell.

panse of liquid between the open ends of the two silica tubes is, of course, negligible relative to the resistance encountered in the narrow silica tubes.

As shown in Fig. 2, the graphite current lead and the graphite current probe in each silica tube are kept separate by encasing the current lead in a small silica protection tube which is open at top and bottom. This protection tube is sealed to the inside of the larger silica tube. Slight indentations near the bottom of the protection tube and the larger silica tube prevent either graphite rod from sliding below the end of the protection tube. This gives a constant measurement, regardless of any small displacements of the electrodes, because the geometry of the cell is now determined completely by the silica tubing alone. Due to the very low coefficient of thermal expansion of silica, the cell constant is essentially independent of temperature.

Dense alundum and silica served as excellent nonconducting refractories. Graphite proved to be unique as a good conducting refractory for the highly corrosive molten sulphides. However, the graphite rods had to extend to the cool zone of the furnace before wire leads could be attached to them because the carbon formed low melting alloys with any wires contacting it in the hot zone of the furnace.

Heating was accomplished by an induction furnace with a carbon liner, and temperature was measured with a calibrated Pt — Pt-10 pct Rh

Table I. Composition of Typical Matte Before and After 5 Hr Experiment

	Initial Wt Pct	Final Wt Pct
Cu	39.9	39.9
Ni	40.0	40.0
Fe	20.5	20.1
S	27.5* (24.6 actual analysis)	27.9* (22.6 actual analysis)
	100.0	100.0

* Sulphur obtained by difference.

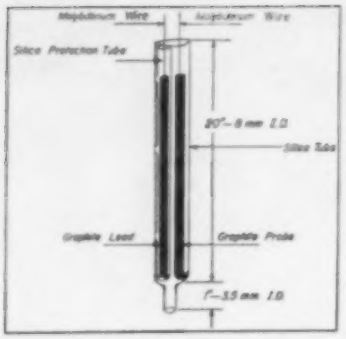

Fig. 2—Detail of electrodes in matte conductivity cell.

thermocouple which was shielded from the molten matte by an alundum protection tube. The cell was kept in a helium atmosphere to prevent oxidation of the molten sulphide.

The Circuit: A diagram of the ac potentiometer circuit for measuring the resistance of the conductance cell is given in Fig. 3. Approximately 120 v single-phase ac current is stabilized to 117 v by a Raytheon voltage regulator which supplies power to the Jackson audio-oscillator, the amplifier, and the oscillograph. The signal from the variable frequency audio-oscillator, which is usually about 0.2 amp at 2 v, is amplified to about 2 amp at 1.5 v in the power amplifier. The current then passes in series through a standard noninductive resistance and the conductance cell. The potential drops, V, across the standard resistance and across the conductance cell are measured in arbitrary units on the vertical sweep of the oscillograph. The resistance of the cell is computed from

$$R_c = R_s \cdot V_c/V_s.$$

R_c and R_s should be of the same order of magnitude to obtain the best precision.

In order to avoid inductance, capacitance, and antenna effects, all wires carrying high frequency current must be shielded carefully, and the circuit must be grounded as shown in Fig. 3. The oscillograph is more suitable for this work than a vacuum-tube voltmeter, because it can detect experimental difficulties by showing the wave form of the current when it is on horizontal gain. If a pure sine wave is not obtained, it means that some of the graphite electrodes are not contacting the molten matte or that there is an antenna effect.

Experimental Procedure

General: The conductance cell was calibrated at room temperature with a standard sulphuric-acid solution of maximum density (1.223 g per cc or 3.70 molar) whose specific conductance is 0.8135 ohm^{-1} cm^{-1} at 24°C. The standard noninductive resistance used in these calibrations was 700 ohms. The cell constant k_c is related to the specific conductance of the acid σ_a and the resistance R_s of the cell containing the acid by $k_c = \sigma_a R_s$, and a typical value for the cells used was about 100 cm^{-1}. This constant is thought to be essentially unchanged at the high temperatures of operation because of the very low coefficient of thermal expansion of silica (see previous section on apparatus).

Chemically pure Cu_2S powder and commercial-grade FeS lumps were weighed out and prefused under a helium atmosphere in a graphite crucible. Of course, a certain small amount of desulphurization will result, as discussed in the section on con-

trols. This departure from stoichiometric conditions means that the system must be considered as at least a ternary. The resulting solid was broken up into lumps to be charged to the alundum crucible of the conductance cell. This procedure was necessary to insure complete filling of the cell crucible and knowledge of the charge composition. The matte was analyzed chemically for Cu, Fe, and S before and after the conductance experiments.

The alundum crucible, charged with lumps of the matte, was introduced into the induction furnace and the matte was fused in a helium atmosphere. As soon as melting was completed, usually at about 1100°C, the silica-tube assembly containing the graphite electrodes was lowered into the molten matte, and the measurements of cell resistance as a function of temperature were carried out as discussed in the description of the circuit. The specific conductance was computed from the formula $\sigma = k_c/R_c$.

On either heating or cooling, temperature change was sufficiently slow that the measurements (requiring about 20 sec) could be made before there was a perceptible change in the thermocouple reading (not more than 5°C). The specific conductance could not be followed below the solidus temperature in this apparatus because the silica tubes and crucible were always crushed by solidification.

Controls: Desulphurization of the molten mattes was not rapid, less than 10 pct in 5 hr at temperature as shown by the typical analyses given in Table I. The specimens were analyzed for copper by the standard iodimetric technique and iron analyses were obtained by volumetric dichromate titration. Sulphur analyses were carried out by the "evolution" method in which the specimen is treated with HCl to evolve H_2S which is absorbed by ammoniacal $ZnSO_4$. The resulting ZnS suspension is acidified and titrated with standard KIO_3-KI solution to a blue starch end-point. Actually, this method of analysis for sulphur would be expected to give low results because the powdered specimen does not dissolve completely in the HCl. It is estimated that the "evolution" method gives results that are low by several percent. This is shown in Table I which compares the actual analyses with the sulphur compositions obtained by difference. This estimate seems to be borne out by the results of later sulphur analyses by the combustion method in which the sulphur is burned off as SO_2 and absorbed in KIO_3-KI solution in the course of titrating to the starch end point. The difference between the initial and final sulphur compositions (about 2 pct in the typical example of Table I) leads to an estimated desulphurization of less than 10 pct in the process of fusion. From the ternary phase diagram of Fig. 5, this is about as much desulphurization as could occur (in most specimens) in the sulphur-rich phase (whose conductivity was measured and for which analyses are presented).* Further, there was no systematic change in specific conductance as the experiment progressed, indicating that the conductance was not strongly dependent on sulphur concentration. Nevertheless, this point is being carefully checked in a separate research program in which a controlled partial pressure of H_2S is used to obtain essentially constant sulphur activity. It is worthy of note that commercial grades of FeS from various sources gave substantially the same results.

* There sometimes was a small amount of metal-rich phase remaining in the bottom of the alundum crucible.

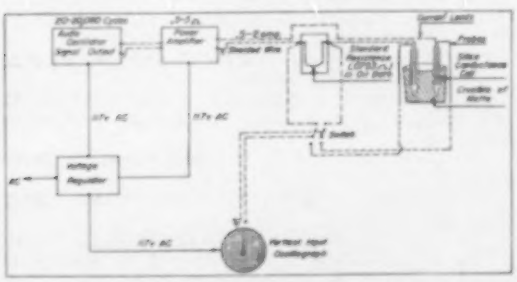

Fig. 3—Electrical circuit for measuring voltage drop across liquid mattes.

It is thought that the concentration of oxygen in the fused specimens was not high because they were prefused in graphite crucibles under a helium atmosphere. Also, the molten mattes were in contact with the graphite electrodes throughout the conductance measurements. In fact, very careful determinations of oxygen by hydrogenation showed that the oxygen content of the specimens was less than 0.5 wt pct.

The results obtained on heating and cooling agreed well within the precision of the experiment (±5 pct), indicating that the measurements were made at nearly constant cell temperatures (±5°C).

Varying the frequency of the current from 400 to 6000 cycles per sec had no appreciable effect on the results. This indicates that there was essentially no capacitance, inductance, or polarization in the conductivity cell. A frequency of 1200 cycles per sec was found convenient and was used in most of the measurements. Variation of the current from 0.5 to 2 amp had no effect on the results, again indicating the Ohm's law behavior of the conductivity cell.

Discussion of Results

The summarized specific-conductance data for molten Cu-Fe sulphide mattes are given in Fig. 4.

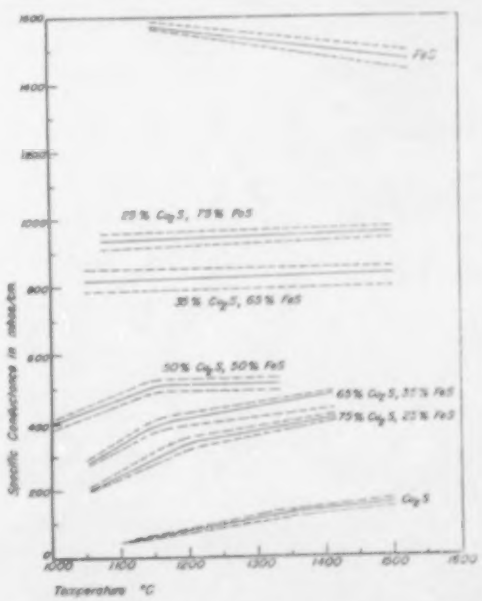

Fig. 4—Summary of specific conductance data for molten mattes. Compositions refer to weight percent.

The solid lines shown here represent the best fit for the data on each nominal composition indicated, while the dashed lines include all of the experimental points (about 100 for each composition). Each nominal composition included two or more separate runs. The spread of data includes all errors of temperature, composition, and electrical measurements.

In Fig. 4 it is seen that the specific conductance of these molten sulphides is much higher than that of typical molten ionic salts such as NaCl ($\sigma = 4$ ohm^{-1} cm^{-1}). This means that simple ionic conduction is not the principal mode of electrical conduction in the present case.*

* In a separate publication describing the results of electrolysis measurements on molten Cu-Fe sulphides, it will be shown that the ionic conductance in these systems must be quite low.

In this system, molten FeS has the highest specific conductance (about 1500 ohm^{-1} cm^{-1}), and exhibits a small negative temperature coefficient (about −0.00017 per °C), resembling metallic conduction.[10] Molten Cu_2S has the lowest specific conductance (about 100 ohm^{-1} cm^{-1}) and exhibits a small positive temperature coefficient (about 0.003 per °C), resembling semiconduction. Typical chemical analyses of these specimens are given in Table II. These data for molten Cu_2S are essentially in agreement with those of Bornemann[12] but show a somewhat higher temperature coefficient. The molten Cu_2S-FeS mattes are seen to follow a roughly additive rule of mixtures with respect to both specific conductance and temperature coefficient. The breaks in the specific conductance curves for mattes of intermediate composition are explained by a phase change in which the matte (on cooling) separates into metal-rich and sulphur-rich liquid phases. It can be seen from the phase diagram of Fig. 5[14] that this would be expected to occur after a small amount of desulphurization.

From these results, it may be concluded that the structure of the molten mattes is neither molecular (as typified by benzene, water, etc.) nor simply ionic (as typified by molten CuCl, $SnCl_2$, etc.). Possibly the interatomic bonds in these liquids are of a metallic nature. At present, the specific volumes of the mattes are being estimated as a function of composition and temperature to permit calculation of the molar conductance σ_M. This molar conductance data then will be analyzed to investigate the more quantitative aspects of the hypothesized electronic conduction mechanism and the apparent semiconduction in the Cu_2S-rich mattes.*

* The results of conductivity experiments on molten Cu_2S-CuCl and molten Cu-S systems of varying Cu/S ratio will be presented in a separate publication.

Table II. Composition of Molten Sulphides after Conductance Experiments

		Wt Pct
Typical FeS Specimen	Fe	63.3
	S	36.7* (31.7 actual analysis)
		100.0
Molar ratio, Fe/S		0.99
Typical Cu_2S Specimen	Cu	80.4
	S	19.6* (18.2 actual analysis)
		100.0
Molar ratio, Cu/S		1.03

* Sulphur obtained by difference.

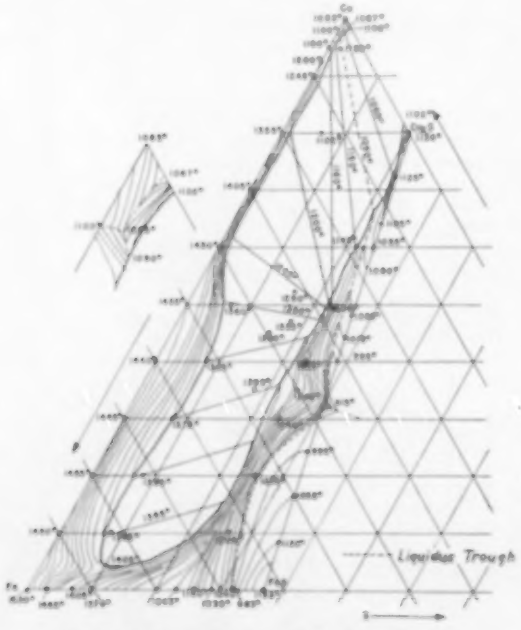

Fig. 5—Liquidus projection of the system Cu-Fe-S.

Acknowledgments

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venient in treating the system to use the standard

the compound $2CaO \cdot SiO_2$ which is very stable and

Activities in the Iron Oxide-Silica-Lime System

by John F. Elliott

PRESENT knowledge of the usual metallurgical slags indicates that they are, for the most part, rather complex in behavior and as yet there is no ready means for describing, in a simple manner, the behavior of any one of them. One of the best known slag systems is the iron oxide-silica-lime ternary which is the basic "solvent" in a number of important metallurgical refining operations, the basic open hearth being one of the most important. In this operation, the slag dissolves such components as sulphur, phosphorus, manganese oxide, and magnesia. Considerable study of this slag system and the behavior of these additions has been carried out in the past by a number of authors, as has been summarized in several critical reviews.[1, 2] However, except for determination of the activity of iron oxide, only a limited amount of effort has been directed towards developing, from these data, an understanding of the general behavior of the basic solvent.

Reported here are the results from a series of calculations based on data from the literature which permit a semiquantitative evaluation of the activities of iron oxide, silica, and lime (plus magnesia) in the ternary system at 1600°C. The preliminary results, which were reported briefly at a symposium held by AIME in 1953,[3] have been revised and are completed. The steps in the calculation are as follows:* 1—establish the activity curves and the curve of the excess molar free energy of mixing at 1600°C for each of the binary systems, 2—construct the activity surface of iron oxide for the ternary from the data on the binary systems and information available in the literature for the ternary area, 3—determine the surface of excess molar free energy of mixing for the ternary system from the activity surface of iron oxide and from the molar curves obtained for the binary system, and 4—differentiate the ternary surface of the molar excess free energy of mixing to obtain the ternary surfaces for the logarithm of the activity coefficients for silica and lime (log γ_{SiO_2} and log γ_{CaO}).

* The thermodynamic symbols used here are those conventional in American texts, i.e., see S. Glasstone.[4] As examples, a is activity, $\gamma = a/N$ or activity coefficient, and the superscript x designates an excess quantity (actual minus ideal). All the compositions are given as mol fractions.

SiO_2-Fe_tO: Schuhmann and Ensio[5] have measured the activity of iron oxide in simple iron oxide-silica slags when in equilibrium with γ iron. Their data recalculated to 1600°C are shown in Fig. 1. Also included is a point representing a measurement by Gokcen and Chipman[6] of the activity of iron oxide at 1600°C at the point of saturation with solid silica. For convenience and in accordance with other treatments,[7] the calculations are based on the hypothetical component, Fe,O, which is obtained by converting all the analyzed iron in the slag to FeO. In spite of Schuhmann and Ensio's conclusion that the activity of iron oxide in the system does not vary with temperature over the experimental range of 1258° to 1407°C, the data are corrected to 1600°C assuming that temperature does have an effect. It was felt to be most reasonable to assume that the term log γ_{Fe_tO} is a linear function of the reciprocal of the temperature. Rey[8] has indicated that an effect of temperature on the activities in this system is to be expected from the Schuhmann and Ensio data. In essence, the correction consists of multiplying the experimental value of log γ_{Fe_tO} by the ratio of the experimental temperature in Kelvin to 1873°K. The magnitude of the correction is not large, being approximately 11.5 pct of the experimental value of log γ_{Fe_tO}.

A very minor correction was necessary to compensate for the fact that the slags were in equilibrium with γ iron in the experiment, while at steelmaking temperatures they would be in equilibrium with liquid iron. Data for the correction were obtained from Darken and Gurry.[9] The standard states established are pure liquid iron oxide (Fe_tO) in equilibrium with pure liquid iron (with the appropriate amount of oxygen in solution) and pure liquid silica.

The method of plotting in Fig. 1 is convenient for the calculation of the activity of liquid silica and permits a reasonable extrapolation for the activity of Fe,O in the ranges where no experimental data are available. The uncertainty in the extrapolation to infinity at one terminal where $N_{Fe_tO} = 1$ for the usual Gibbs-Duhem integration is reduced considerably by this method. The region of two coexisting liquid phases is estimated to range from 1.8 to 41.7 mol pct Fe,O. The nature of the activity curve for the single-phase region indicates that the activity of iron oxide across the two-phase region is very close to 0.39. Computation of the function log $\gamma_{Fe_tO}/(1-N_{Fe_tO})^2$ for this region (dashed line) in conjunction with the curve through the adjusted experimental data indicate the best probable value of 0.382 for a_{Fe_tO} in the two-phase area. The line from 0 to 0.018 N_{Fe_tO} is obtained by assuming that the component follows Henry's law. In this range, the value for log γ_{Fe_tO} is 2.59. Appropriate mathematical manipulation of the plotted line† yields the activity curves for the system as shown in Fig. 2, A.

† See ref. 9 where this method is treated in some detail.

The curve ΔF^x, the excess molar free energy of mixing (actual minus ideal), as shown in Fig. 3 is also computed from Fig. 1. This curve is required for subsequent calculations.

CaO-Fe_tO: The phase diagram for the lime-iron oxide system when in equilibrium with liquid iron is not well known but there appears to be no intermediate compound present. This fact as well as the activity values for Fe,O extrapolated to the CaO-Fe,O binary from Taylor and Chipman[7] tend to indicate somewhat negative deviations from ideality for the activity curves for the two components. Strong indication of this is evident in Fig. 1 where are plotted the points computed from the estimated activities of Fe,O for the binary system.[7] It appears that the best line through the data is a horizontal straight line. Because of the general indication of the slight negative departure from ideality, the line is extrapolated horizontally to $N_{Fe_tO} = 0$. It is con-

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venient in treating the system to use the standard state of the pure liquid for each component and thereby avoid the two-phase area of the lime-saturated slag. Fig. 2, B shows the computed activity curves for this system and Fig. 3, B shows the curve of ΔF°. The limiting activity coefficients (γ°) are 0.12.

As a check on the calculations of the properties of the CaO-Fe_xO system, it is possible to estimate the activity of liquid lime at the point of lime saturation by a somewhat unrelated method. Rossini et al.[10] give the free-energy change for the reaction

$$CaO_{(s)} \rightleftarrows CaO_{(l)};\ \Delta F = 12{,}000 + 4.2\,T \qquad [1]$$

near the melting point of 2600°C. Assuming that this equation is valid down to 1600°C, the ratio of the activity of pure solid lime to that of pure liquid lime at 1600°C is 0.33. In the binary system at the point of saturation of the slag with solid lime, the activity of lime in the liquid slag must be equal to that of pure solid lime. Thus, relative to the standard state of pure liquid lime, both the lime in solution and solid lime in equilibrium have an activity of 0.33. The fact that this point lies close to the calculated curve for the activity of liquid lime tends to support the method of calculation used here.

CaO-SiO_2: The phase diagram for the lime-silica system, which is rather well known, is dominated by the compound $2CaO \cdot SiO_2$, which is very stable and which has a high melting point. Darken[12] has calculated the molar curve of $\Delta F/4.576\,T$ for the binary system of liquid lime and liquid silica. His method was used to repeat this calculation to obtain the curve of $\Delta F^{\circ}/4.576\,T$ (Fig. 3) for the binary from the ternary activity surface of Fe_xO as shown in Fig. 4. Although Richardson[11] also has determined the curve for the lime-silica system, Darken's was used instead, since it is more consistent with the activity curves for Fe-O in the ternary field. In the binary system, the excess molar free energy of mixing (ΔF°) is equal to $4.576\,T\ (N_{SiO_2} \cdot \log \gamma_{SiO_2} + N_{CaO} \cdot \log \gamma_{CaO})$.

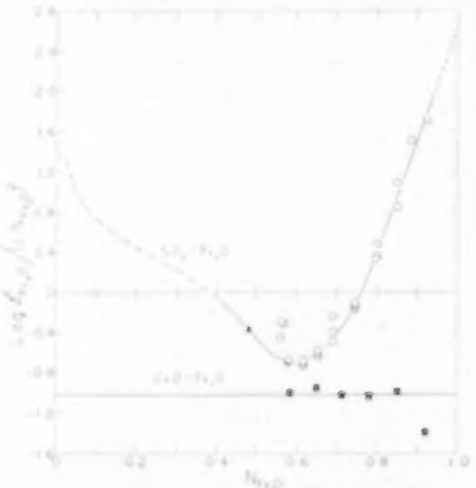

Fig. 1—Free-energy functions at 1600°C for the liquid binary system. Open circle is the data of Schuhmann and Ensio,[9] modified; triangle, Gokcen and Chipman,[7] and closed square, after Taylor and Chipman.[1]

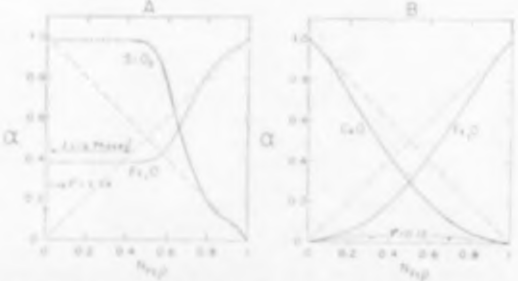

Fig. 2—Activity curves at 1600°C for the liquid binary systems. *A* is CaO-Fe_xO, after Schuhmann and Ensio.[9] *B* is SiO_2-Fe_xO. Open circle in *B* is from thermal data.[10]

Ternary System

Activity of Fe_xO: The iso-activity lines for Fe_xO in the ternary system as shown in Fig. 4 constitute in essence a contour map. The lines are based on the activity data for Fe_xO reported by Taylor and Chipman.[1] Additional points for slags which were low in manganese oxide and phosphorus were calculated from Winkler and Chipman.[13] The iso-activity lines are extended to the extremities of the diagram as required by the activity curves of the binary system, CaO-Fe_xO and SiO_2-Fe_xO (Fig. 2). The iso-activity lines were extended across the region of the two coexisting liquid phases on the basis that the tie lines extend radially and would converge at the silica apex if there were virtually no solubility of iron oxide in liquid silica. This arrangement appears reasonably sound because the two-phase regions in the bordering binary systems extended about equal distances from the silica apex. It is to be noted that the activity of each component is constant across a tie line in the two-phase area.

The iso-activity lines were drawn as smoothed curves through the data and to the sides. Because the basic data assumed the same behavior for MgO and CaO in this system, the ternary system is actually Fe_xO-SiO_2-(CaO + MgO). To provide a con-

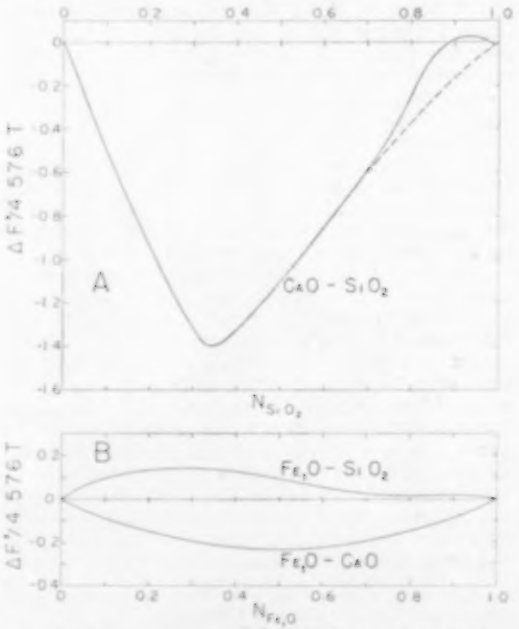

Fig. 3—Excess free-energy curves at 1600°C for the liquid binary system. *A* is CaO-SiO_2, after Darken[12] and *B* is SiO_2-Fe_xO and CaO-Fe_xO.

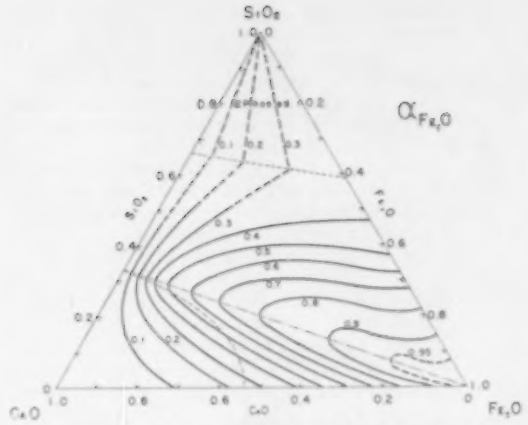

Fig. 4—Iso-activity curves for Fe_xO at 1600°C for the liquid Fe_xO-SiO_2-(CaO + MgO) ternary system, after Taylor and Chipman[7] and Winkler and Chipman.[16]

Fig. 5—Excess molar free energy of mixing surface for the liquid Fe_xO-SiO_2-(CaO + MgO) system at 1600°C.

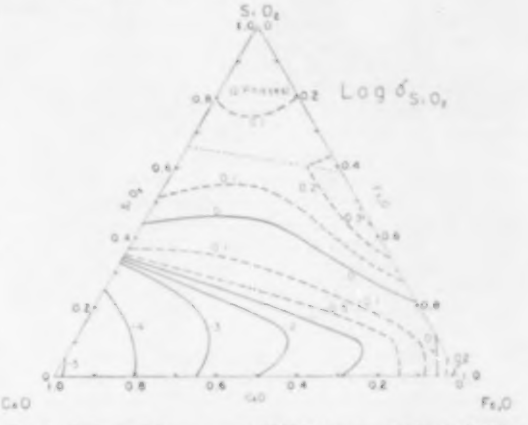

Fig. 6—Surface of log γ_{SiO_2} at 1600°C for the liquid Fe_xO-SiO_2-(CaO + MgO) system.

sistent pattern thermodynamically for the arrangement of the iso-activity lines, activity curves for the pseudobinary lines, as follows, were constructed: $CaO/SiO_2 = 4/1$, $CaO/SiO_2 = 2/1$, $CaO/SiO_2 = 1/1$, $CaO/SiO_2 = 1/2$, and $CaO/SiO_2 = 1/4$. Smoothed curves of a_{Fe_xO} were also drawn for lines of constant N_{Fe_xO} at 10 pct intervals. These sets of curves were used to aid in interpolating the activity lines. To ensure thermodynamic consistency to the plot, curves of $\Delta F°/4.576\ T$ were computed for the five pseudobinary lines and the surface of $\Delta F°/4.576\ T$ obtained is shown in Fig. 5.

Slight adjustment of the activity lines in the remote corners of the ternary system was necessary in order to obtain a fully coordinated set of curves for a_{Fe_xO} and $\Delta F°/4.576\ T$.

Activity of CaO and SiO_2: The surface of $\Delta F°/4.576\ T$ for the ternary system in Fig. 5 was necessary in order that the activity coefficients of silica and lime (plus MgO) could be obtained. Determination of these activity coefficients was accomplished by the slope-intercept method according to the following equation

$$\frac{\log \gamma_2}{4.576\ T} = \frac{\Delta F°}{4.576\ T} + \frac{(1-N_2)}{4.576\ T}\left[\gamma \Delta F°/\gamma N_2\right]_{N_1/N_3}, \quad [2]$$

In this equation, the subscript 3 designates the component Fe_xO. Subscript 2 designates either SiO_2 or CaO and, alternatively, 1 is either CaO or SiO_2. The ratio N_1/N_2 requires that the differentiation be carried out along a line of constant ratio of component 1 to component 3. This is a straight line from apex 2 to the opposite binary 1-3.

Actually, the determinations of the activity coefficients for silica and lime were made graphically. Taking silica as an example, from Fig. 5 a plot of $\Delta F°/4.576\ T$ vs N_{SiO_2} for each of the quasi-binary lines of Fe_xO/CaO of 4/1, 2/1, 1/1, 1/2, and 1/4 was constructed. Then the value of $\log \gamma_{SiO_2}/4.576\ T$ at any given composition for one of the quasi-binary lines was the intercept at the axis of $N_{SiO_2} = 0$ of the tangent to the curve at the selected composition. This graphical method yielded a continuous curve of $\log \gamma_{SiO_2}/4.576\ T$ vs N_{SiO_2} for each of the quasi-binary lines.

Interpolation from curves of $\log \gamma_{SiO_2}$ for the boundary binary systems and the five quasi-binary systems yielded the surface of $\log \gamma_{SiO_2}$ as shown in Fig. 6. The thermodynamic behavior of silica is presented in this way, instead of by iso-activity lines, because there is such a tremendous range in activity from 0.00001 in the region of nearly pure liquid lime to 1 at the silica apex.

The surface of $\log \gamma_{CaO}$ for liquid lime as shown in Fig. 7 was derived from the $\Delta F°/4.576\ T$ surface in Fig. 5 in the same manner as was described for obtaining the surface of $\log \gamma_{SiO_2}$. Once again, the logarithmic function of the activity coefficient is used because the activity of lime varies over a range of from 0.006 to 1.

Discussion

In trying to deduce from known phase diagrams some estimation of the thermodynamic behavior of the components in the iron oxide-silica-lime system, two dominant features are noted: the high stability of dicalcium silicate, ($2CaO \cdot SiO_2$), and the presence of the field of two coexisting liquid phases near the silica apex. That this very strong attraction between lime and silica persists well out towards the Fe_xO apex has been shown by experimentally determined[7, 16] iso-activity lines which are distorted to a pronounced extent along the quasi-binary line between $2CaO \cdot SiO_2$ and Fe_xO. The semiquantitative determination of the behavior of lime and silica in this ternary at steelmaking temperatures indicates that the activities of lime and silica change very

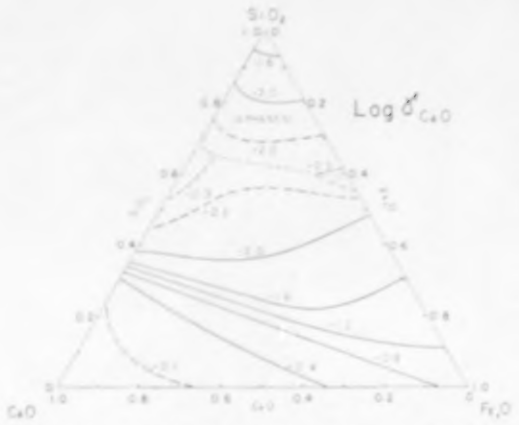

Fig. 7—Surface of log γ_{FeO} at 1600°C for the liquid Fe_xO-SiO_2-(CaO + MgO) system.

abruptly as the region of this quasi-binary line is crossed. Proceeding parallel to the line, a much more gradual change is found.

Rather rigorous thermodynamic methods of calculation have been adhered to here because, as pointed out by Darken,[16] they permit a reasonably reliable representation of the properties of the system where extrapolations are required. These are required in the areas near the liquid lime and liquid silica apexes. It is felt that, although the resultant surfaces describing the behavior of lime and silica are semiquantitative, they do aid in giving the reader a "feel" for the basic behavior of the metallurgical slags which stem from this system.

Turkdogan and Pearson[18] have depicted the activity surface for FeO for the ternary system FeO – (CaO + MnO + MgO) – (SiO_2 + P_2O_5). Their results are generalized from quite a number of experimental studies. The surface which they drew differs somewhat from Fig. 4 in that the extension of the iso-activity lines for FeO towards the acids-bases binary side is not along the quasi-binary line of bases to acids of 2/1 but is distorted towards the bases corner. It is to be noted that this same difference is present in comparison with the basic results of Taylor and Chipman.[7] This apparently results from Turkdogan and Pearson's[18] use of information obtained from a number of complex slag systems. Their diagram may be more convenient for representing the behavior of iron oxide in the complex slags than is Fig. 4. However, the method of establishing the surface for a_{FeO} is not as rigorous thermodynamically as is carried out here nor does it permit the ready calculation of the behavior of lime and silica in the ternary system.

It is hoped that these data will stimulate further thought on means for depicting the behavior of the components of metallurgical slags. While the general separation of species into acids, bases, and oxidizers has been very useful and successful, it is considered to be only partially satisfying from the thermodynamic point of view in interpreting this system. The treatment of slags by the ionic theory also has been reasonably successful. The necessity of establishing a priori the species to be treated is, however, somewhat unsatisfactory thermodynamically. It is considered that the approach presented here could lead to describing the behavior of an additional component to the basic ternary system by a plot over a portion of the ternary field of some such device as iso-activity coefficient lines. This would avoid the need for artificially assumed species of various sorts. For example, in a paper to be published soon, the behavior of MnO in steelmaking slags is approximated by contour lines of constant γ_{MnO} over a portion of the ternary field.

The results from Figs. 4 and 7 have been somewhat helpful in developing a method for correlating data on dephosphorization obtained during the refining period in basic open hearth operations. The method has been to compute the equilibrium constant for the reaction of iron oxide and lime in the slag with phosphorus in the bath to produce phosphorus pentoxide dissolved in the slag. Attempts to correlate data reported by Winkler and Chipman[14] have been only partially successful. Further computations now being made will be reported later.

Summary

Data reported in the literature on various parts of the iron oxide-silica-lime system have been correlated and surfaces of a_{FeO}, log γ_{SiO_2}, and log γ_{CaO} at 1600°C for the liquid ternary system have been computed. The pure liquid has been selected as the standard state for each component. The results, which are semiquantitative, are best summarized by reference to Figs. 4 through 7.

Acknowledgments

The author acknowledges the help of Mr. Frank Luerssen in performing some of the necessary calculations. He also is grateful to the management of Inland Steel Co. for permission to publish this paper.

Discussion of this paper, if any, will appear in JOURNAL OF METALS, November 1955, and in AIME Metals Branch *Transactions*, Vol. **203**, 1955.

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aime NEWS

Fairless Works To Be Visited By Steel Conference Registrants In April

THE 38th Blast Furnace, Coke Oven and Raw Materials and National Open Hearth Conferences April 18, 19, and 20 will feature an inspection trip through the Fairless Works of the U. S. Steel Corp. Chartered buses will leave the Bellevue-Stratford Hotel, Philadelphia, Wednesday, April 20 at 9:00 am and will return about 4:00 pm. A box lunch will be served by the company during the return bus trip. A charge of $4.00 will be made by the Conference Committees to help defray the plant trip transportation and other nontechnical expenses.

Adequate hotel facilities will be provided at the Bellevue-Stratford Hotel and other Philadelphia hotels. Hotels, however, will not hold blocks of rooms after April 1. Hotel reservation requests should be made directly to the hotel selected.

The registration fee for either Conference is $7.00, which includes a copy of the respective Proceedings, when printed. There is no registration fee for students at any of the sessions, unless they want a copy of the Proceedings. AIME members are entitled to a $2.00 reduction in the registration fee upon presentation of their membership card.

Preliminary Program of Blast Furnace, Coke Oven, And Raw Materials Conference

SUNDAY, APRIL 17

3 to 9 pm
Registration

MONDAY, APRIL 18

8 am to 5 pm
Registration

9:30 am
Agglomeration and Raw Materials Session:
Welcoming remarks. Grading of Minnesota ores for blast furnace consumption; sinter practice at Ford Motor Co. sintering plant; permeability of sinter plant feed; productivity of the conventional Dwight-Lloyd sintering machine; production and properties of experimental pellet sinter.

2:00 pm
Blast Furnace Operations Session:
Production and use of iron coke; 100 pct sinter burden at Gary Works; making self-fluxing sinter and its use in the blast furnace (Domnarfvet, Sweden); stove cleaning.

TUESDAY, APRIL 19

8 am to 5 pm
Registration

9:30 am
Joint Session:
Effect of hot metal on open hearth heat time; use of open hearth slag in the blast furnace and effect on open hearth practice; discussion of mutual problems of open hearth and blast furnace operators.

9:30 am
Coal and Coke Session:
Coke oven to measure expansion pressure; relation of charge density of coal to carbonizing behavior; statistical quality control in coke plant.

12:30 pm
Luncheon Meeting:
Everyone attending the Blast Furnace, Coke Oven, and Raw Materials sessions is invited to attend this luncheon and annual business meeting.

2:00 pm

Coal and Coke Session:
Practical aspects of coal quality; additional products from coal chemicals operation; recent European progress in carbonization.

2:00 pm

Blast Furnace Theory Session:
Solid movement in blast furnace models; reduction of iron oxide from slag by liquid iron; factors affecting desulphurization in the blast furnace; desulphurization of iron as influenced by alloying elements and CO pressure.

6:30 pm

Reception

7:00 pm

Annual Fellowship Dinner
Speaker: A. H. Williams, President, Federal Reserve Bank of Philadelphia.
Toastmaster: C. L. Huston, Jr., President, Lukens Steel Co.

WEDNESDAY, APRIL 20

8 am to 4 pm

Registration

9:00 am

Plant trip

Preliminary Program of National Open Hearth Steel Conference

SUNDAY, APRIL 17

8 to 9 pm

Registration

MONDAY, APRIL 18

8 am to 5 pm

Registration

10:00 am

General Session:
Welcoming remarks. Announcements. McKune Award paper.

10:30 am

Hot Metal Basic Operations Session:
Decreasing scrap charging time; effect of nozzle pocket block and autopour on production and quality; reduction of bank and bottom delays by bath temperature control.

10:30 am

Acid Operating Session:
Economics of acid open hearth production; sand survey.

2:00 pm

Refractories and Masonry Session:
All basic furnace construction; modified slopes of port roofs; special refractories for checker brick; gun maintenance of backwalls, skews, and roof.

2:00 pm

Operating Metallurgy Session:
Residual metals in steel, 1954; rimming action observed by motion pictures; influence of ingot size on segregation in rim steel; special hot topping practices.

TUESDAY, APRIL 19

8 am to 5 pm

Registration

9:30 am

Joint Session:
Effect of hot metal on open hearth heat time; use of open hearth slag in the blast furnace and effect on open hearth practice; discussion of mutual problems of open hearth and blast furnace operators.

9:30 am

Cold Metal and Basic Foundry Session:
Pouring small molds with large ladles; comparison of open hearth and electric furnace operating costs in a cold metal plant; atomization of fuel oil with high pressure gas; combustion practice using 100 pct natural gas; metallurgical control in a cold metal shop; chemical cleaning of checkers; bottom pouring for surface quality.

2:00 pm

Operating and Combustion Session:
Controlled firing rates; use of large amounts of high pressure coke oven gas; use of large amounts of low pressure coke oven gas; atomization with natural gas; oxygen steelmaking in Canada.

6:30 pm

Reception

7:00 pm

Annual Fellowship Dinner
Speaker: A. H. Williams, President, Federal Reserve Bank of Philadelphia.
Toastmaster: C. L. Huston, Jr., President, Lukens Steel Co.

WEDNESDAY, APRIL 20

8 am to 4 pm

Registration

9:00 am

Plant trip

European Meeting Lays Stress On Personal Contacts

The Arc de Triomphe in Paris.

PLANS for the Joint Metallurgical Societies Meeting in Europe June 1 to 19 will place the accent on personal contact rather than formal presentation of prepared papers.

With plant excursions emanating from London, Düsseldorf, Liege, and Paris, AIME members will have an opportunity to talk over mutual problems with people schooled in European technological development.

Just what will the meeting cover? Program scope will encompass ironmaking (including coke and ore preparation), steelmaking, mechanical working and heat treatment, both ferrous and nonferrous (including hot and cold rolling, forging, wire drawing and continuous casting, but not the foundry industry), refining and fabrication of nonferrous metals, heat treatment, surface treatment (including finishing and coating), metallurgical education and training in industry, and research.

A plenary session has been planned for each country visited but discussion groups will provide the main vehicle. European societies are appointing group leaders to guide discussion. In addition to the fact that these group leaders are recognized authorities, there will be leading experts available to participate in the talks.

Dusseldorf's convention hall.

Trips have been arranged to the largest and most modern metallurgical establishments in Great Britain and on the Continent. Tours available to participants while in England include works of Stewarts & Lloyds Ltd.; Enfield Rolling Mills Ltd.; and several alternate research organizations. Other British Isles tours take in South Wales, Birmingham, Sheffield, Scunthorpe, Durham, Yorkshire, and various installations in Scotland.

Resurgent West Germany and its industry will be on display in a first hand showing. Technical visits to plants and laboratories, talks with the men who brought about the rebirth of German production, and a look at German methods are on the agenda.

From Düsseldorf, the itinerary will take delegates to Liege, Belgium, where visitors can see the plant of the Soc. Anon John Cockerill. Another tour is planned for the new laboratories of Centre National de Recherches Metallurques at l'Abbay du Val-Benoit.

And then on to Paris where the opening plenary session will be at the Sorbonne or the University of Paris. Technical visits in and near Paris include: Centre d'Etude de Chimie Metallurgique at Vitry; Centre Technique des Industries de la Fonderie, at Sevres, Jasquet Hispano-Suiza at Bois-Colombes; and Conservatoire des Arts-et-Metiers, Paris.

Travel Arrangements

There are still openings on the delegation from the U. S. However, those wishing to go are urged to make their intentions known quickly. Travel arrangements are by Thomas Cook & Son. Cost of the basic tour, including first class passage is about $1500. Information on accreditation, industrial visits, steamer and air transportation, and hotel reservations may be obtained by writing Ernest O. Kirkendall, Secretary, American Committee, 29 West 39th St., New York, N. Y., or Thomas Cook & Son.

American participation in the meeting is under joint sponsorship of the AIME and ASM. Co-Chairmen of the American Committee are Leo F. Reinartz and James B. Austin.

A great many technical trips have been planned and are available as alternate tours. Transatlantic passage and main tour reservations should be made immediately. Reservations for alternate trips are limited so fast action is required to avoid disappointment.

Despite the heavy technical program, there will be time for a taste of the Europe one reads and hears about. Paris, the City of Light, will be in one of its most gracious, beautiful seasons for the meeting. London, with its history, Buckingham Palace, and Elizabethan pageantry, awaits the tourist. Germany, and its gorgeous countryside, good food, and castles on the Rhine are certain to induce freetime roaming.

The Landseer Lion in London's Trafalgar Square.

Pacific Meeting Plans Progressing

Plans for the Pacific Northwest Regional Conference to be held in Spokane on April 28, 29, and 30 are progressing nicely according to A. Y. Bethune, Sullivan Mining Co., Kellogg, Idaho, General Chairman.

Frank N. Marr, president, Spokane-Idaho Mining Co., has accepted Chairmanship of the Committee on General Arrangements in

A. Y. BETHUNE
General Chairman

Spokane, handling all facilities at the Davenport Hotel, headquarters for the conference, as well as other matters such as registration, finance and publicity. Working with him will be Karl Jasper, president, Grandview Mines, and Hamilton Owen of the Spokane Chamber of Commerce.

W. M. Armstrong, dept. of mining and metallurgy, University of British Columbia, Vancouver, has been appointed as Chairman of the Div. of Physical Metallurgy and Lee W. Heinzinger, metallurgical supervisor, Bethlehem Pacific Coast Steel Co., Seattle, Wash., has been appointed Chairman of the Div. of Iron and Steel for the conference sessions.

F. R. Morrall reports that one of the features of the conference will be a symposium on X-ray fluorescent analysis. This program is planned to be of interest to most members of the AIME such as geologists, mining engineers, chemists, extractive and physical metallurgists, and anyone interested in industrial minerals and minerals beneficiation.

A technical session Saturday morning will be followed in the afternoon by a demonstration session on X-ray fluorescent analysis. In the morning technical session there will be a brief description of the principles of the method. This will be followed by a discussion of analytical precision and statistical aspects of metallurgical plant control. The speakers will present actual data on the application of X-ray fluorescent technique to mineral and metallurgical products, and its application to industrial hygiene and toxicology. X-ray fluorescent analysis results will be given on soil, ores, concentrates, tailings, slags, and alloys. The speakers at the technical session will be F. A. Hames, head of the dept. of metallurgy at the Montana School of Mines, Butte, Mont., D. M. Mortimore, head of the physics laboratory, Bureau of Mines, Albany, Ore., and P. A. Romans, also of the Albany Bureau of Mines.

Among the specific topics to be discussed will be tungsten ores, concentrates and tailings, hafnium in zirconium ores, and production plant products, columbium, tantalum, uranium, thorium, and various rare earth elements in the complex ores. Materials related to more common metals will also be presented.

In the afternoon apparatus will be on display to demonstrate X-ray fluorescent analysis techniques and to run samples for interested parties.

Apr. 15, 1955 is the deadline for papers that are to be presented at the Institute of Metals Div. Fall Meeting in Philadelphia, Oct. 17 to 19, 1955. Papers received by this deadline but requiring revision may not be processed in time to permit scheduling for this meeting.

Send Coupon For New AIME Directory

During the month of June, a new all-Institute Directory will be issued. This publication will contain an alphabetical and geographical listing of all members on the Institute records, Feb. 1, 1955. In addition, the Directory Supplement listing all officers, Branches, Divisions, Local Sections, Student Chapters, and committee personnel will be included with this volume.

However, increased costs for producing this type of material have made it necessary to alter the procedure of past years. The Directory will be mailed only to those members in good standing who request it by filling out and mailing the coupon.

This is most important, as requests by letter will not be acknowledged. Each request for the Directory must be made with the coupon. Subsequent announcements will be made concerning the Directory, but the coupon appearing in this issue of the magazine will be the only valid requisition for the book. Fill in the coupon and mail to AIME, 29 West 39th St., New York 18, N. Y.

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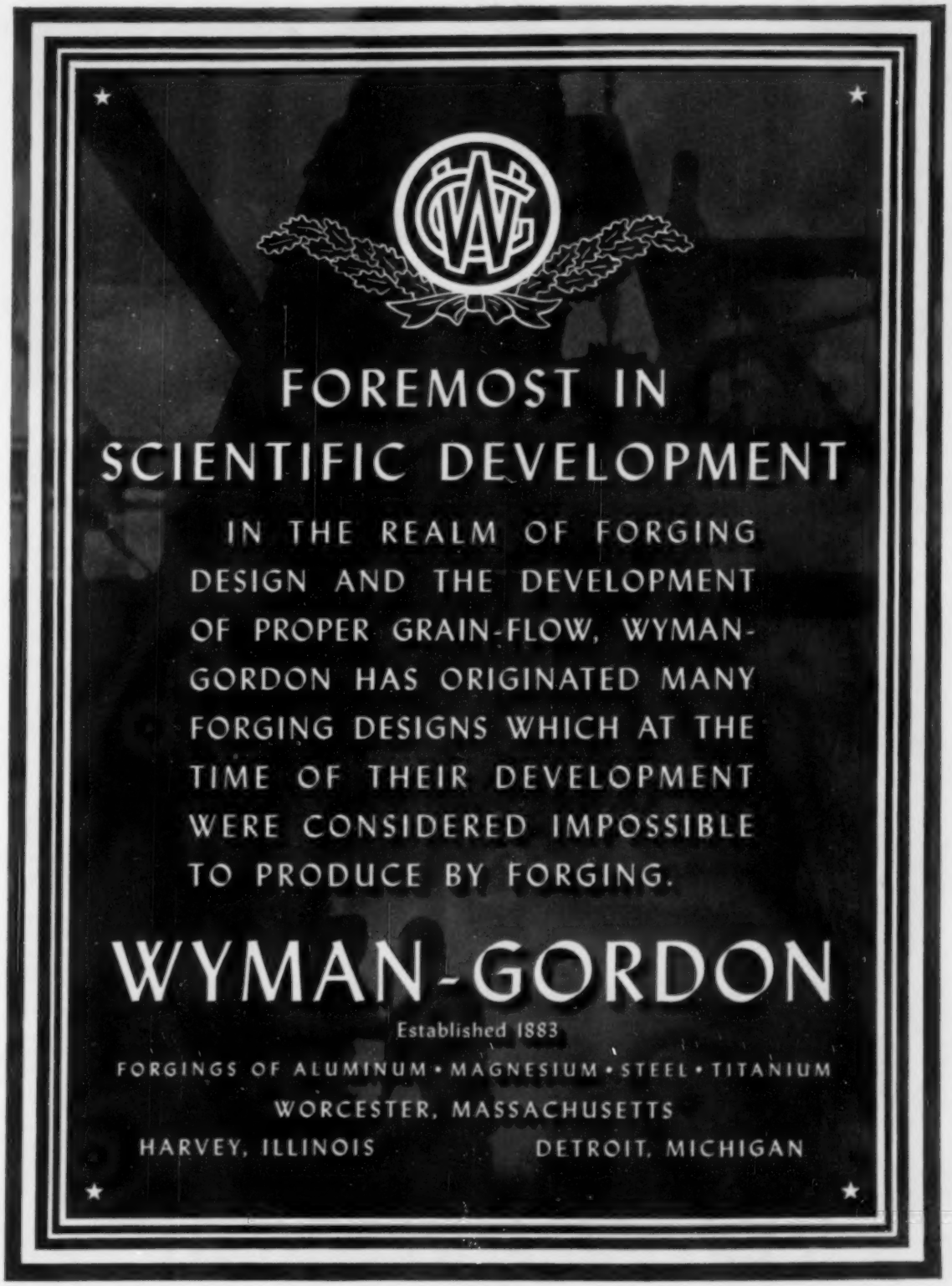
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SCIENTIFIC DEVELOPMENT
IN THE REALM OF FORGING DESIGN AND THE DEVELOPMENT OF PROPER GRAIN-FLOW, WYMAN-GORDON HAS ORIGINATED MANY FORGING DESIGNS WHICH AT THE TIME OF THEIR DEVELOPMENT WERE CONSIDERED IMPOSSIBLE TO PRODUCE BY FORGING.
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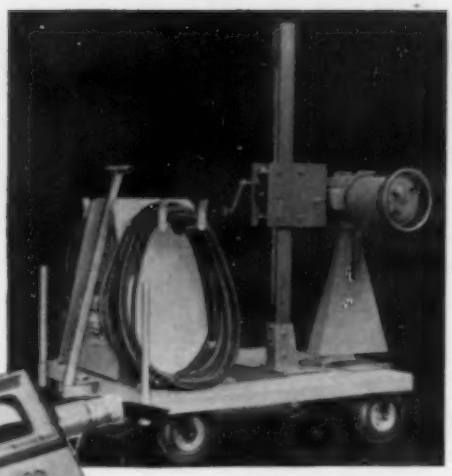
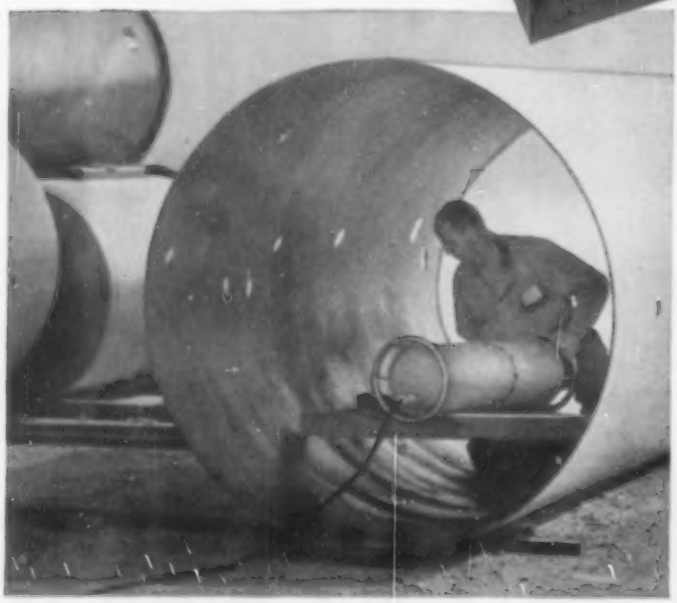
Compact, versatile x-ray inspection unit

goes where the job is



Here's one of the ten mounts available for OX-175. It's a mobile truck with elevating tube stand.

Sturdy control cabinet measures 18 x 18 x 14 inches . . . features large, easy-to-read dials, pinpoint accuracy of operation.



Shown here is inside-out x-ray inspection of a vessel weld.

General Electric OX-175 can help you cut costs . . . improve quality

Opening new horizons for industry in the use of x-ray inspection is General Electric's new OX-175. This rugged, lightweight apparatus handles the widest working range ever covered by a single x-ray unit.

The OX-175 can be easily moved from one job to the next, and its 200 feet of cable gives it extra portability. Highly versatile, the OX-175 can be equipped with angle-target tube for 60° field of radiation. With flat-target tube it will produce a 360° field of radiation that will radiograph an entire circumferential weld in one exposure. This also permits simultaneous radiographing of a large number of castings or assemblies by grouping these around the tube head.

In addition, the small size of the tube head makes it ideal for inside-out radiography . . . giving greater radiographic coverage, better radiographs, and reducing protective needs.

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GENERAL ELECTRIC

Personals

William B. Nelson, Great Lakes Corp., has been transferred from New York to Waltoria, Calif.

John A. Bara has joined the atomic energy div., Sylvania Electric Products, Inc., Bayside, N. Y., as a metallurgical engineer. He had been on the staff at Battelle Memorial Institute, Columbus, Ohio.

Robert L. Kamm has resigned from the Wiltshire File Co., Victoria, Australia, and is now associated with the Carboloy dept., General Electric Co., Detroit, Mich.

Herbert M. Meyer has joined the Watertown Arsenal Laboratory, metals research branch, Watertown, Mass. Mr. Meyer had been with the Armour Research Foundation, Chicago, Ill.

V. A. Phillips has resigned from the British Non-Ferrous Metals Research Assn. to accept the position of senior metallurgist in the chemical and metallurgical section of the English Electric Co., Luton Airport, Luton, Bedfordshire, England.

R. R. Lloyd has become process superintendent, Titanium Metals Corp. of America, Henderson, Nev. He had been assistant supervising engineer, U. S. Bureau of Mines, Boulder City, Nev.

A. O. Hall is chief geologist for the American Smelting & Refining Co., Wallace, Idaho.

E. R. Marble, manager of the Tacoma smelter, American Smelting & Refining Co., Tacoma, Wash., has been traveling through the Orient.

Ernest G. Ovitz, Reynolds Metals Co., Salida, Colo., is now located at Benton, Ark.

William J. Jenkins, formerly with the Joy Mfg. Co., Pittsburgh, has joined the staff of the Westinghouse Electric Co., Pittsburgh, Pa.

Frank B. Huke has been appointed chief atomic products engineer, refractories div., Norton Co., Worcester, Mass. Mr. Huke has been associated with the Norton Co. since September 1954.

Michael P. Apostolik has become manager of Wheeling Steel Corp.'s New York district sales office. He succeeds **Harold W. Schroeder** who recently retired after 39 years with the company. Mr. Schroeder was retained as a consultant.

William H. Kinney has been appointed resident metallurgical engineer for the Kaiser Steel Corp., Oakland, Calif.

Robert F. Renkin has been named research and development engineer for the Sharon Steel Corp., Sharon, Pa. **George D. Meyers** who was superintendent of hot strip finishing div. since 1950 now has been named superintendent of coating in addition.

William W. Lamb was appointed sales manager, Precision Metalsmiths, Inc., Cleveland, Ohio. He succeeds **R. W. Evans,** who was named vice president and treasurer.

Leonard C. Schmidt has been named works manager in charge of tooling and production activities at Worcester Pressed Steel Co., Worcester, Mass.

M. S. Gokhale, RCA Victor div., RCA is the 1955 president of the Standards Engineers Society, Camden, N. J. **Herbert G. Arlt,** Bell Telephone Laboratories, has been elected vice president.

Robert L. Wright has been appointed industrial designer, sales and product planning, General Electric Co., laminated and insulating products dept., Pittsfield, Mass.

Clarence B. Sampair was elected to the board of directors, Minnesota Mining & Mfg. Co., St. Paul, Minn.

Eugene A. Leary is presently employed at the Pratt & Whitney Aircraft div., United Aircraft Corp., East Hartford, Conn., as a development metallurgist.

Joseph M. Denney has been appointed a research associate in the metallurgy dept., General Electric Research Laboratory, Schenectady, N. Y. Dr. Denney had been a research engineering consultant with the North American Aviation Co.

Raymond H. Capps and **Aubrey M. Kirby** have joined the staff of the Electro Metallurgical Co.'s metals research laboratories, Niagara Falls, N. Y.

Clayton L. Davis was appointed technical service director of the Universal Atlas Cement Co., New York, N. Y.

Nelson M. McGuire was recently appointed assistant to the vice president of sales, American Manganese Steel div., American Brake Shoe Co., Chicago, Ill.

Douglas C. Lynch, formerly executive vice president of Brush Electronics Co., Cleveland, has been named president.

B. J. Osborne has been appointed assistant to the vice president and general manager, Kaiser Steel Corp., Oakland, Calif.

Roy D. Palmer, formerly associated with the Aluminum Co. of America and Aluminium Ltd., has joined Loewy-Hydropress Co., New York, N. Y., as industrial consultant.

Herman E. Bakken, assistant general manager, Aluminum Co. of America, refining div., has been named general manager of the division. He succeeds **A. B. Williams** who is retiring as general manager.

George Bennethum has been appointed assistant manager of tool steel sales for the Carpenter Steel Co., Reading, Pa. Prior to his promotion Mr. Bennethum was a sales representative in Cleveland.

Lloyd V. Guild has been elected vice president in charge of research and product development, Burrell Corp. Mr. Guild has been with the firm since 1941 as research director.

Necrology

Date Elected	Name	Date of Death
1921	David Atkins	Unknown
1921	Crosby F. Baker	Dec. 9, 1954
1918	J. J. Cadot	Jan. 19, 1955
1916	G. Lister Carlisle	Dec. 22, 1954
1914	John A. Dresser	Unknown
1937	W. R. Ellis	Jan. 20, 1955
1939	David E. Green	Dec. 1, 1954
1918	Vladimir A. Grodsky	Jan. 6, 1955
1953	Robert L. Hardy	Dec. 29, 1954
1945	Harman G. Lichtenstein	Unknown
1943	John T. Parker	Jan. 12, 1955
1928	W. W. Simon	Jan. 11, 1955
1890	James Underhill	Unknown

Proposed for Membership

— Metals Branch AIME —

Total AIME membership on Dec. 31, 1954 was 21,816; in addition 2179 Student Associates were enrolled.

ADMISSIONS COMMITTEE

O. B. J. Fraser, Chairman; R. B. Caples, Vice-Chairman; F. A. Ayer, A. C. Brinker, R. H. Dickson, Max Gensamer, Ivan A. Given, Fred W. Hanson, T. D. Jones, Sidney Rolle, J. H. Scaff, John T. Sherman, F. T. Sisco, Frank T. Weems, R. L. Ziegfeld.

The Institute desires to extend its privileges to every person to whom it can be of service, but does not desire as members persons who are unqualified. Institute members are urged to review this list as soon as possible and immediately to inform the Secretary's office if names of people are found who are known to be unqualified for AIME membership.

In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; A, Associate Member; S, Student Associate.

Alabama
Birmingham—Gearhart, Thomas A. (A)

Arizona
Phoenix—Feuerstein, William (J) (R. C/S—S-J)

California
Grass Valley—Shull, Charles M., Jr. (A)
Oakland—Gottstein, Jay S. (J)
San Jose—Anderson, James H. (M) (R. M)
Wilmington—Middleton, Glenn E. (A)

Colorado
Arvad—Pettit, Frank P. (M)
Denver—Huffman, Mervin G. (M)

Connecticut
Nichols—Bohn, Edw. L. (A)
Riverside—Hogue, Robert S. (M) (R. C/S—S-M)
Wallingford—Willhelm, Arthur C., Jr. (M) (C/S—A-M)

Delaware
Wilmington—Hix, Hugh B. (A)

Illinois
Chicago—Yaeger, Charles J. (M)
Collinsville—Sackett, Byron E. (J)
Forest Park—Garner, Paul B. (A)
Homewood—Dyer, Harry B. (M) (C/S—A-M)
Lemont—Kelman, LeRoy R. (M) (R. C/S—S-M)
Northlake—Finch, David A. (M)
Riverside—Aamodt, Herbert C. (A)
Urbana—Lieberman, David S. (J)

Indiana
East Chicago—Gentz, Robert S. (M)
New Castle—Torr, Melvin J. (A)
Whiting—Hendricks, Lester L. (A)

Maryland
Baltimore—Bozman, Richard L. (M)

Massachusetts
Needham—Cairns, Raymond E., Jr. (J)
South Lincoln—Shank, Maurice E. (M) (C/S—A-M)

Michigan
Birmingham—Olson, John H. (M) (C/S—A-M)
Muskegon—Lener, Eugene J. (A)

Missouri
Ferguson—Hug, Allan E. (A)
Joplin—Schutz, Howard W. (M) (C/S—A-M)

Nevada
Boulder City—Fuller, Harry L. (M)
Henderson—Davis, Claude M. (M)
Reno—Winston, John S. (M) (C/S—A-M)

New Jersey
Jersey City—Holmes, Tunis L. (A) (R. C/S—J-A)
Mendham—Manzone, Mario G. (M)
Newark—Green, Robert B. (M)
Riverton—Hendren, Robert R. (A)

New York
Buffalo—Clough, William R. (M)
Grand Island—Shortsleeve, Francis J. (M)
Lockport—Emery, Charles H. (J)
New York—Frenkel, Robert Ed. (J)
New York—Nanda, Madan M. (J) (R. C/S—S-J)
Niagara Falls—Korczynsky, Michael (M)
Schenectady—McMullin, John (M) (C/S—A-M)
Tonawanda—Marshall, Darwin (A)

Ohio
Barberton—Oros, George J. (A)
Canton—Capuano, Anthony (A)
Canton—Dye, Wilmer A. (A)
Canton—Peterson, Leland D. (A)
Cincinnati—Stewart, Alexander, Jr. (M)
Cincinnati—Westermann, Fred E. (M) (C/S—A-M)
Cleveland—Morris, J. Howard, Jr. (A)
Cleveland—Rodgers, William (M)
Cleveland—Stone, Harry D. (A)
Columbus—Keeler, John R. (M) (R. C/S—J-M)
Ironton—Rickey, James H., Jr. (A)
Newark—Cunningham, James W. (M) (C/S—A-M)
Niles—Moorhead, Paul E. (J)
Solon—Graham, Glenn R. (M)
Warren—Weimer, Clark H. (M)
Willoughby—Wilkie, Keith G. (M) (C/S—A-M)

Oregon
Albany—Deardorff, Donald K. (M)

Pennsylvania
Beaver—Wallace, William W. (A)
Beaverdale—O'Donnell, John M. (J)
Bethlehem—Bigge, Henry C. (A)
Brackenridge—Shaw, Richard B. (A)
Johnstown—Mullen, Gerald R. (A)
Library—Webster, Richard R. (M)
Milton—Dye, Joseph R. (A)
New Kensington—Pacter, Michael V. (A)
Oil City—Pearson, John B. (A)
Oreland—Jefferis, Philip P. (A)
Pittsburgh—Brashores, Creighton A. (A)
Pittsburgh—Casey, Samuel B., Jr. (A)
Pittsburgh—Follansbee, John H., Sr. (A)
Pittsburgh—Forsyth, Robert H. (A)
Pittsburgh—Gorman, Henry B. (M) (R. C/S—J-M)
Pittsburgh—Hines, Robert A. (A)
Pittsburgh—Smith, Stanford O. (A) (R. C/S—S-A)
Sewickley—Walton, Thomas M., Jr. (A)
Stoystown—Bittner, Robert W. (M)

Utah
Kearns—Knudson, Charles B. (A)
Salt Lake City—Leigh, Arthur H. (M) (C/S—A-M)

Washington
Pullman—Zelezny, William F. (M) (R. C/S—S-M)

Wisconsin
Grafton—McDowell, Stanley E. (A)

Canada
Alberta—Haworth, John B. (J) (R. J)
Trail—Hargrave, James H. D. (M)
Vancouver—Armstrong, William M. (M)
Windsor—Chappell, James N. (A)

France
Paris—Bensimon, Roland L. (M)

Japan
Osaka—Toshio, Tanaka (M)
Tokyo—Yoshitsugu, Mishima (M) (C/S—A-M)

Norway
Oslo—Hansson, Per C. (M) (C/S—A-M)

Sweden
Nynashamn—Lundgren, Gosta T. (M)

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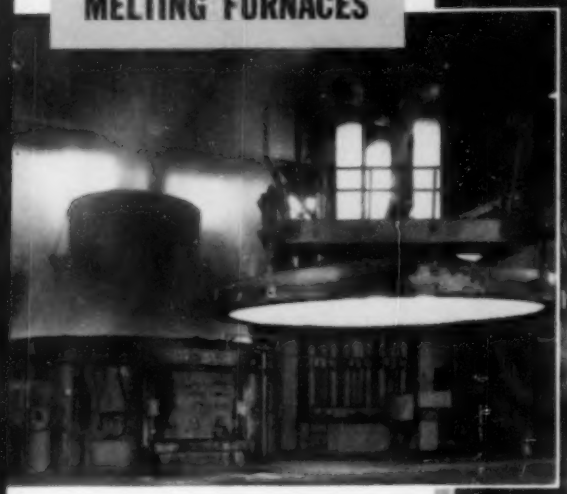

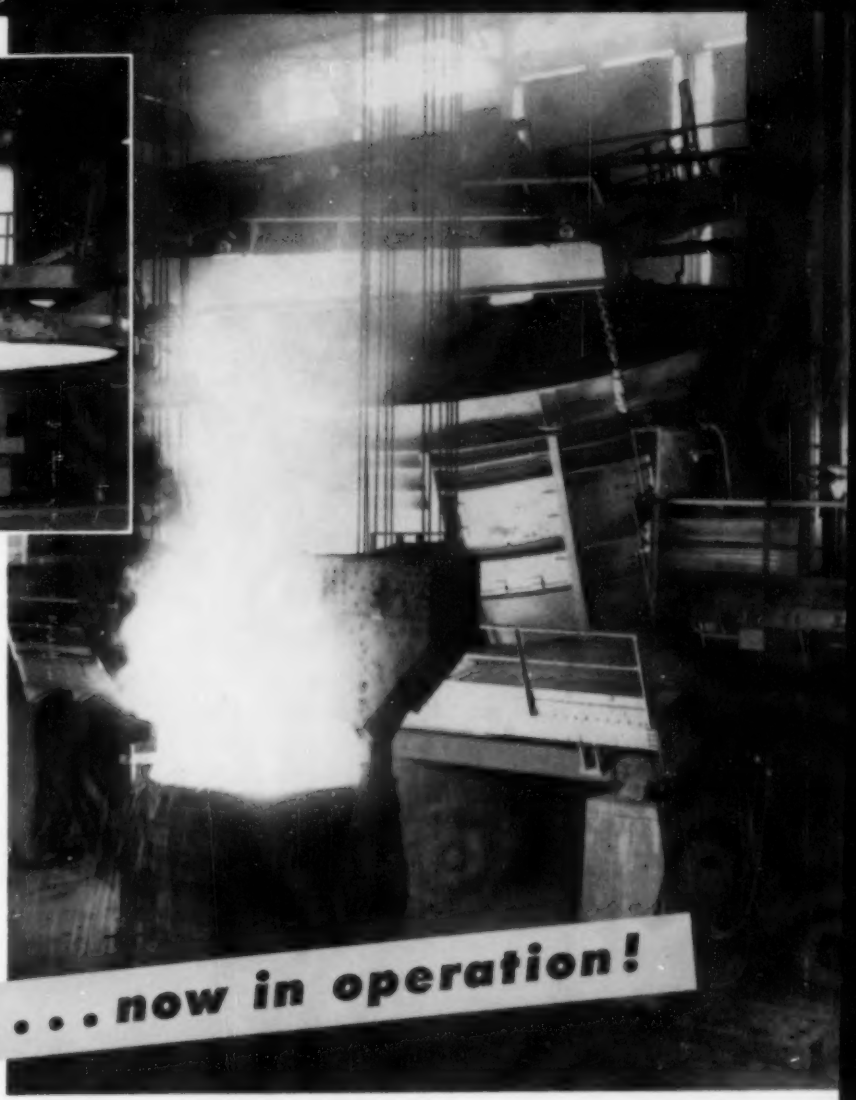

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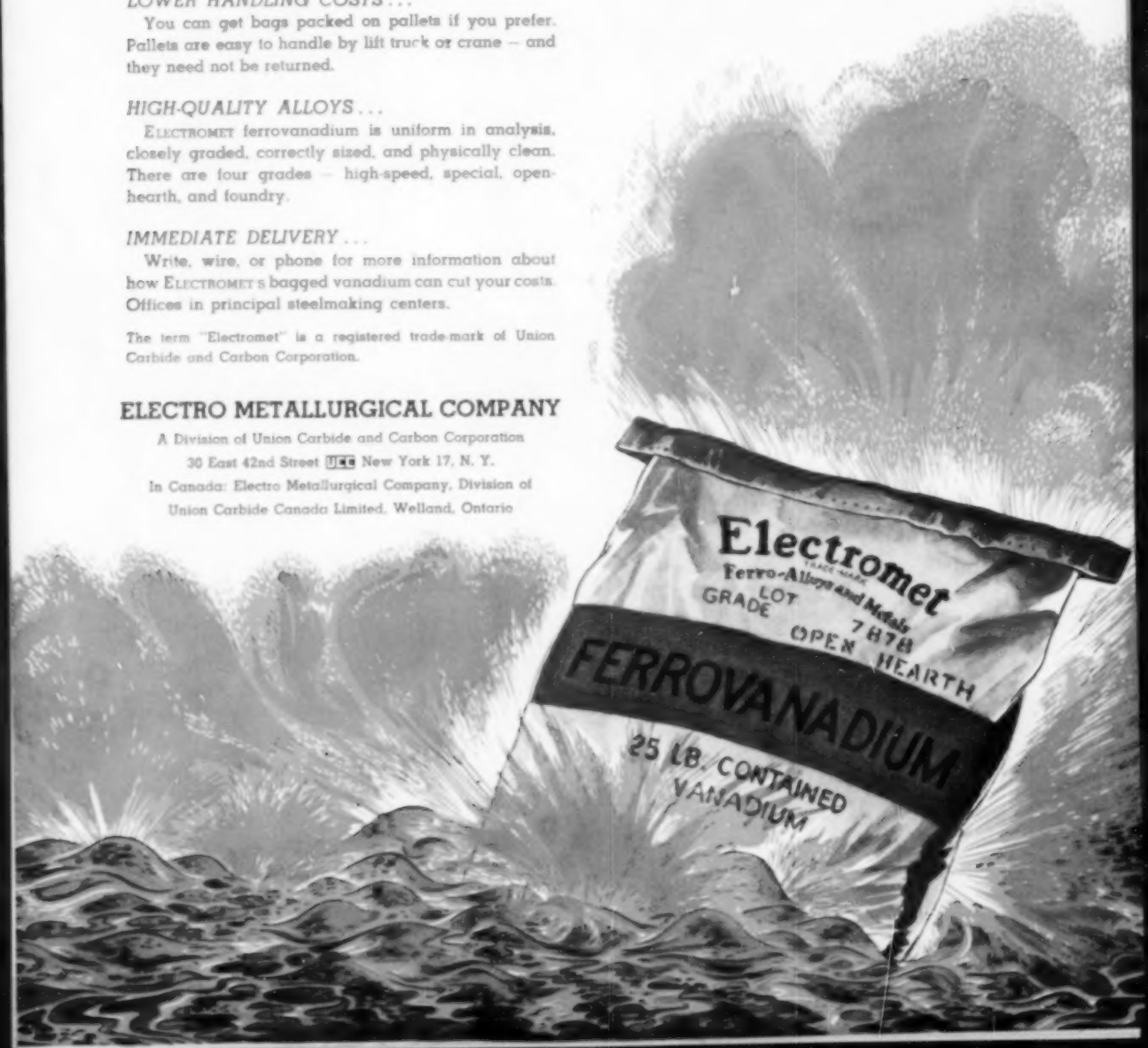
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